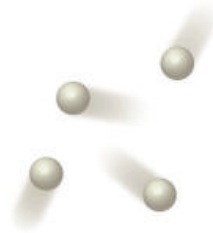


Chapter Two

Structures of Solids

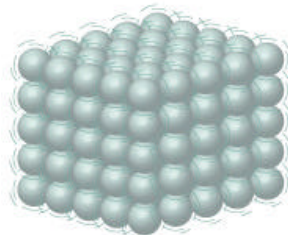
States of Matter Compared



Gas



Liquid



Solid

Table 2.11 Comparison of intermolecular and intramolecular interactions

| <i>Type of interaction</i> | <i>Example</i> | <i>Energy of interaction between molecules or units</i> |
|--|---|---|
| Dispersion (Instantaneous dipole-induced dipole) | H ₂ (bp 20 K) CH ₄ (bp 112 K) CCl ₄ (bp 350 K) CF ₄ (bp 112 K) <i>n</i> -C ₂₈ H ₅₈ (mp 336 K) | ~0.1–5 kJ/mol or ~10 (T _{bp} K) J/mol |
| Dipole-induced dipole | Xe(H ₂ O) _x solvation of noble gases or hydrocarbons (see text) | |
| Ion-induced dipole | Ions in a molecular matrix (see text) | |
| Dipole-dipole | NF ₃ —NF ₃ (bp 144 K) BrF—BrF (bp 293 K) | 5–20 kJ/mol |
| Ion-Dipole | K(OH ₂) ₆ ⁺ Ions in aqueous solution and solid hydrates | 67 kJ/mol (energy per bond) |
| Hydrogen bond | (H ₂ O) _x , (HF) _x , (NH ₃) _x alcohols, amines HF ₂ [−] | 4–50 kJ/mol for neutral molecules |
| Cation-anion | NaCl, CaO | 400–500 kJ/mol of MX “molecules” |
| Covalent bond | H ₂ F ₂ Cl ₂ Li ₂ | 432.08 kJ/mol 154.6 kJ/mol 239.32 kJ/mol 100.9 kJ/mol |

Some Characteristics of Crystalline Solids

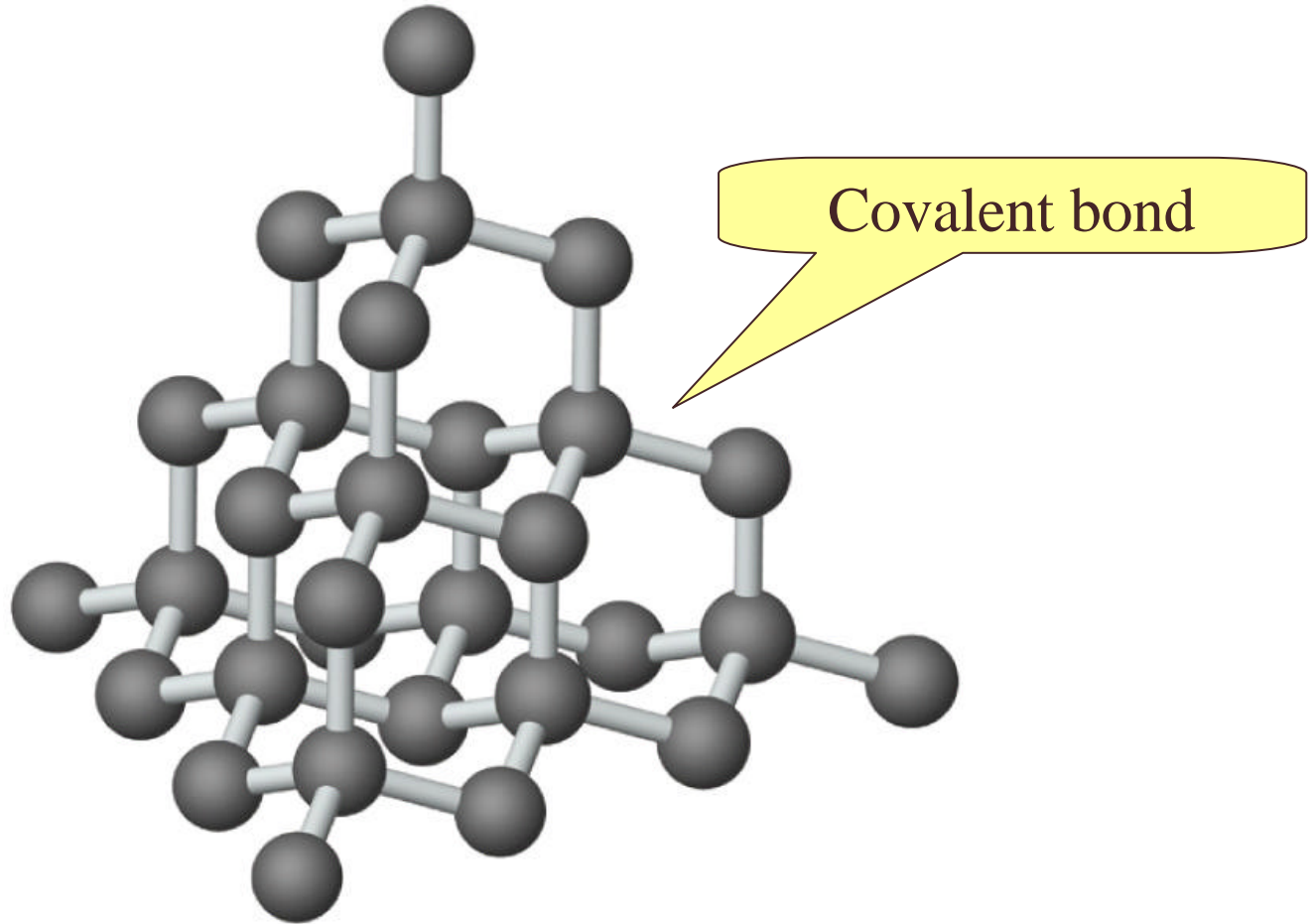
TABLE 11.5 Some Characteristics of Crystalline Solids

| Type | Structural Particles | Intermolecular Forces | Typical Properties | Examples |
|-------------------------|---------------------------------------|--|---|--|
| Molecular | | | | |
| <i>Nonpolar</i> | Atoms or nonpolar molecules | Dispersion forces | Extremely low to moderate melting points; soluble in nonpolar solvents | Ar, H ₂ , I ₂ , CCl ₄ , CH ₄ , CO ₂ |
| <i>Polar</i> | Polar molecules | Dispersion forces, dipole-dipole and dipole-induced dipole attractions | Low to moderate melting points; soluble in some polar and some nonpolar solvents | HCl, H ₂ S, CHCl ₃ , (CH ₃) ₂ O, (CH ₃) ₂ CO |
| <i>Hydrogen-bonded</i> | Molecules with H bonded to N, O, or F | Hydrogen bonds | Low to moderate melting points; soluble in some hydrogen-bonded and some polar liquids | H ₂ O, HF, NH ₃ , CH ₃ OH, CH ₃ COOH |
| Network Covalent | Atoms | Covalent bonds | Most are very hard; sublime or melt at very high temperatures; most are nonconductors of electricity | C(diamond), C(graphite), SiC, SiO ₂ , BN |
| Ionic | Cations and anions | Electrostatic attractions | Hard; brittle; moderate to very high melting points; nonconductors as solids, but electrical conductors as liquids; many are soluble in water | NaCl, CaF ₂ , K ₂ S, MgO |
| Metallic | Cations and delocalized electrons | Metallic bonds | Hardness varies from soft to very hard; melting points vary from low to very high; lustrous; ductile; malleable; good to excellent conductors of heat and electricity | Na, Mg, Al, Fe, Cu, Zn, Mo, Ag, Cd, W, Pt, Hg, Pb |

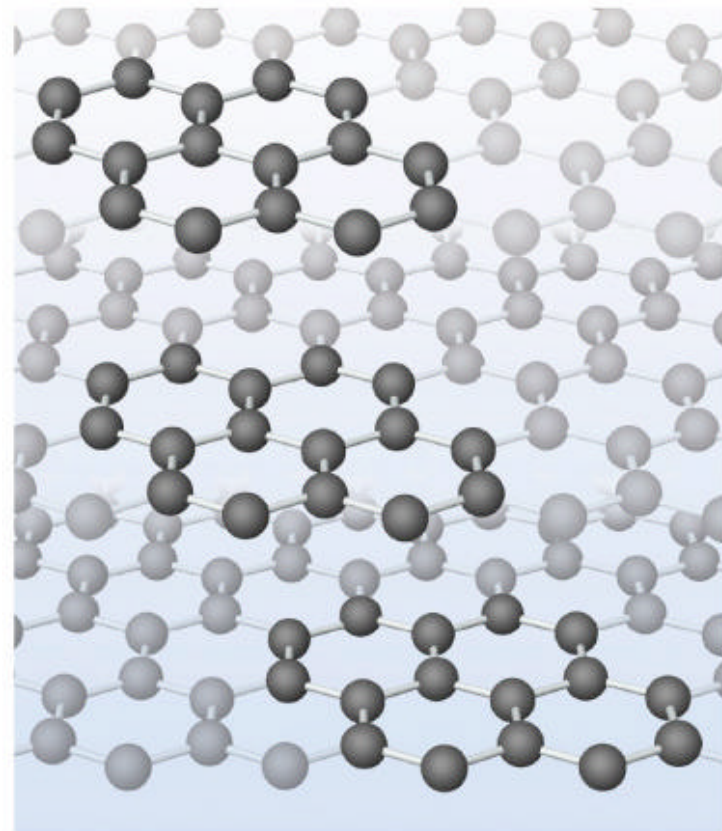
Network Covalent Solids

- These substances contain **a network of covalent bonds** that extend throughout a crystalline solid, holding it firmly together.
- In material science, polymorphism is the ability of a solid material to exist in more than one form or crystal structure. Diamond, graphite and the Buckyball are examples of **polymorphs** of carbon. α -ferrite, austenite, and γ -ferrite are polymorphs of iron. When found in elemental solids the condition is also called **allotropy**.
- The **allotropes of carbon** provide a good example
 1. **Diamond** has each carbon bonded to four other carbons in a tetrahedral arrangement using **sp^3 hybridization**.
 2. **Graphite** has each carbon bonded to three other carbons in the same plane using **sp^2 hybridization**.
 3. **Fullerenes** and **nanotubes** are roughly spherical and cylindrical collections of carbon atoms using **sp^2 hybridization**.

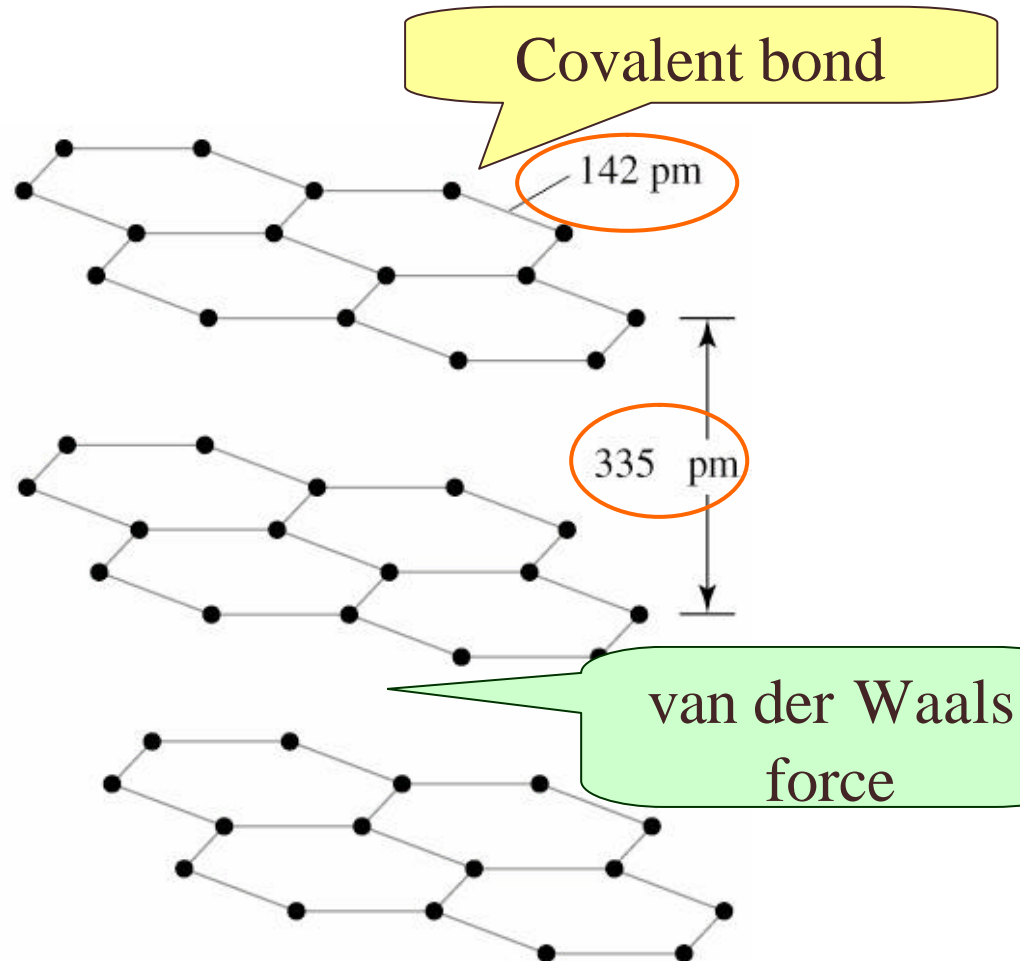
Crystal Structure of Diamond



Crystal Structure of Graphite

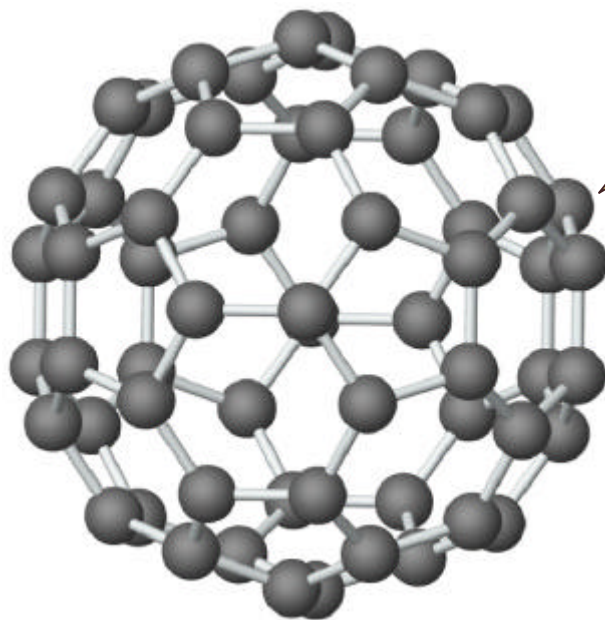


(a)



(b)

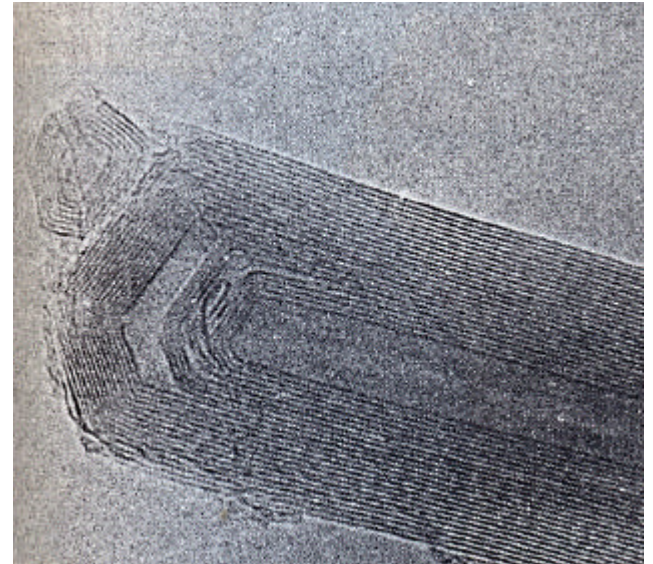
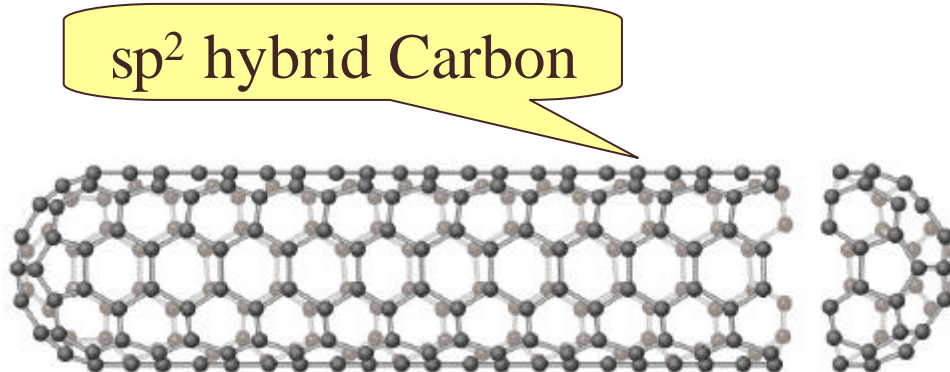
Structure of a Buckyball



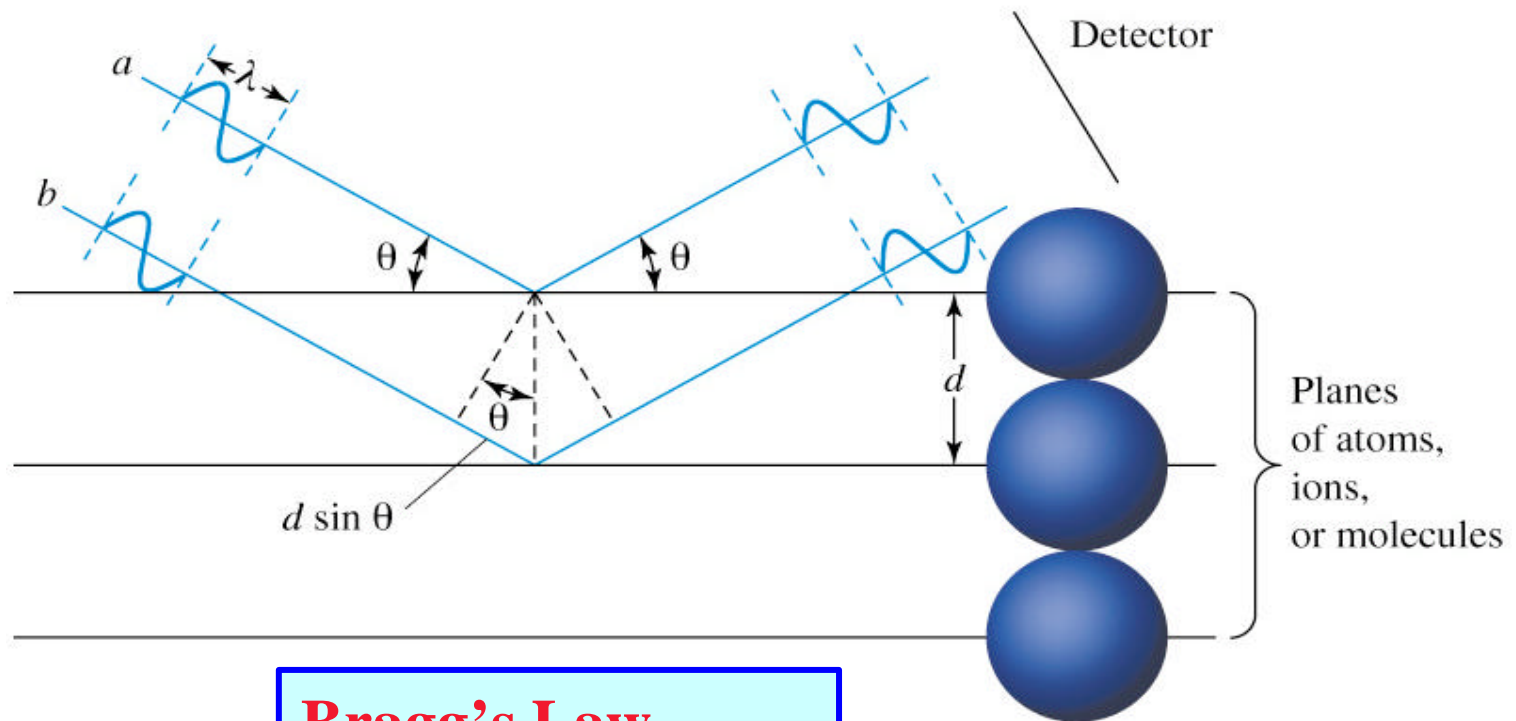
sp^2 hybrid Carbon

Carbon Nano-tube

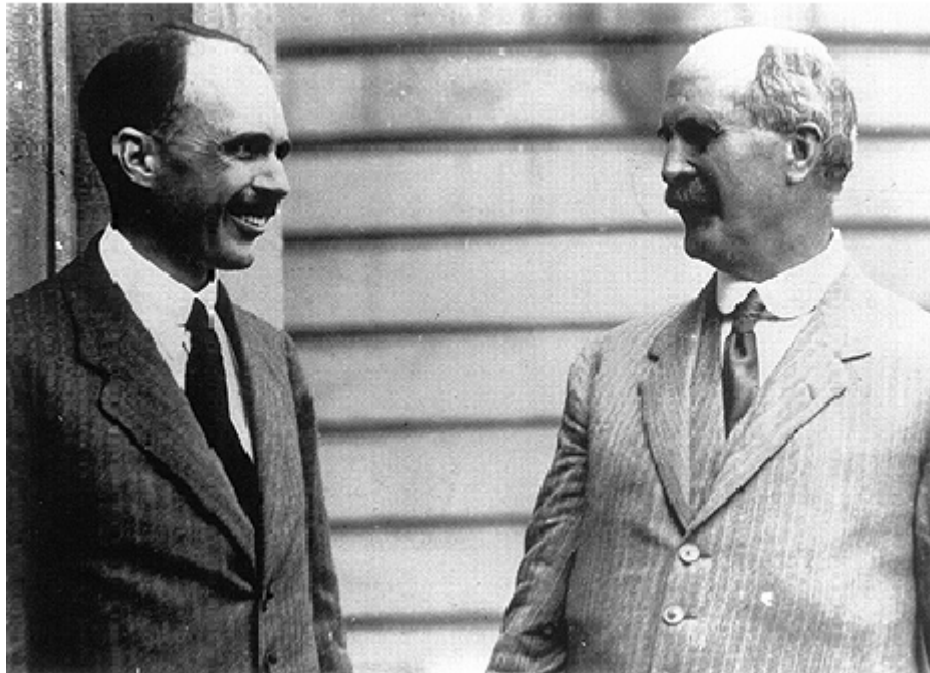
A nanotube (also known as a buckytube) is a member of the **fullerene** structural family, which also includes **buckyballs**. Whereas buckyballs are **spherical** in shape, a nanotube is **cylindrical**, with at least one end typically capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is on the order of a few **nanometers**, while they can be up to several centimeters in length. There are two main types of nanotubes: **single-walled nanotubes (SWNTs)** and **multi-walled nanotubes (MWNTs)**.



Experimental Determination of Crystal Structures



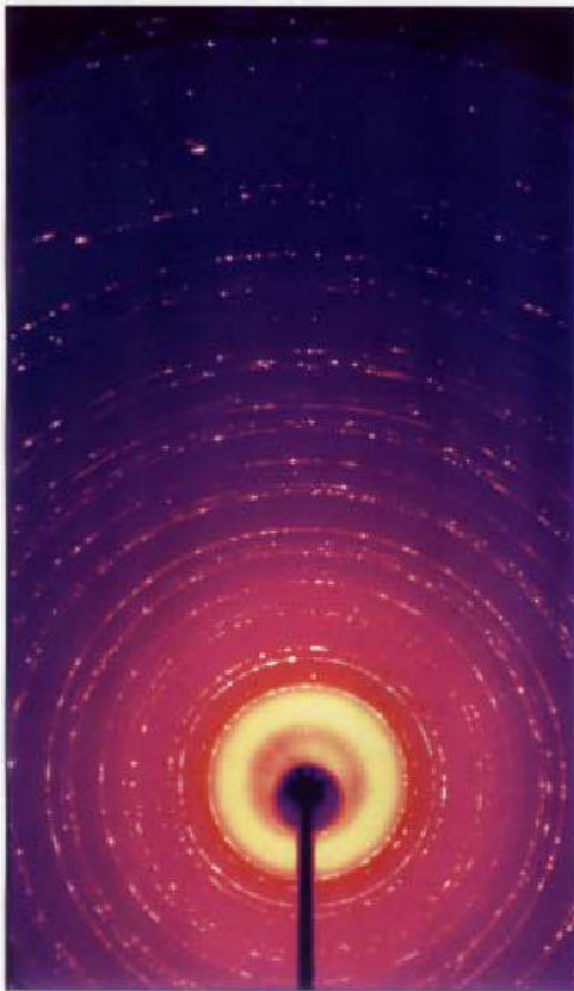
Bragg's Law
 $2 d \sin \theta = n \lambda$



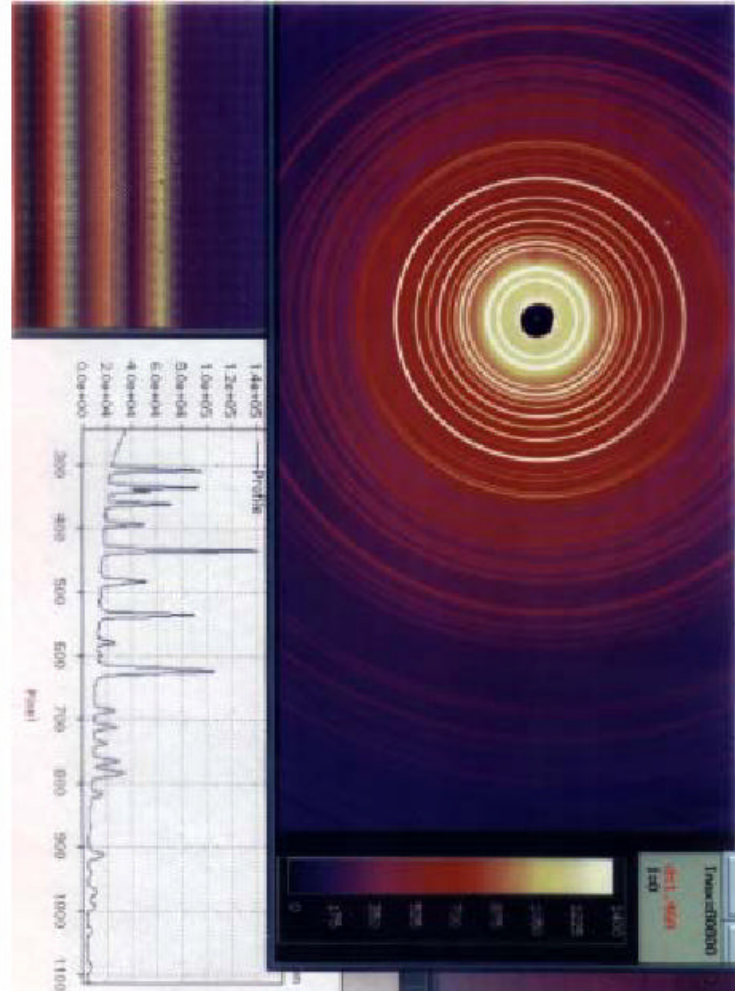
William Lawrence Bragg (left) and William Henry Bragg.

In 1915, Bragg received the Nobel Prize.

X-Ray Diffraction Image & Pattern



Single crystal

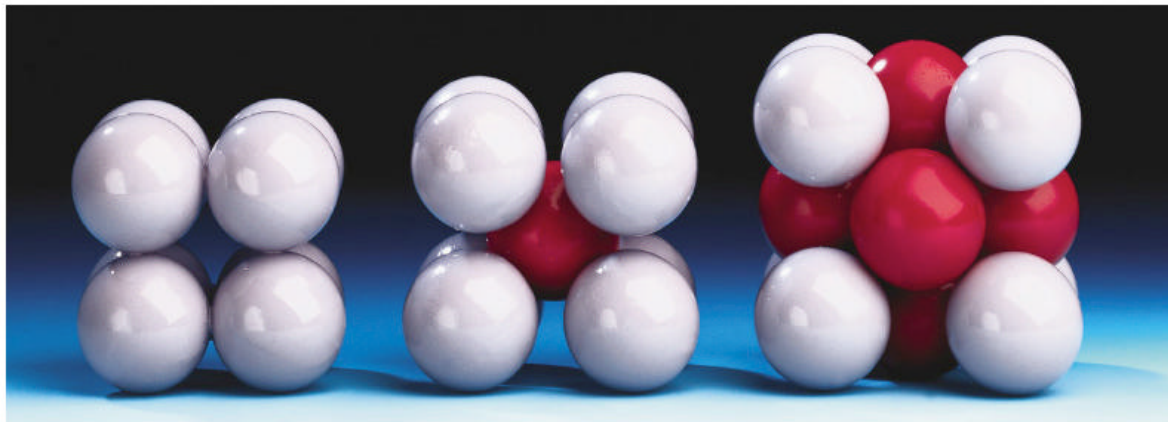
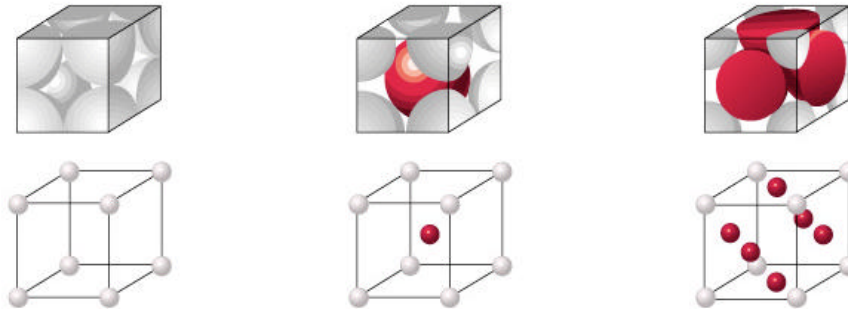


Powder

Crystal Lattices

- To describe crystals, three-dimensional views must be used.
- The repeating unit of the lattice is called the **unit cell**.
- The **simple cubic cell (primitive cubic)** is the simplest unit cell and has structural particles centered only at its corners.
- The **body-centered cubic (bcc)** structure has an additional structural particle at the center of the cube.
- The **face-centered cubic (fcc)** structure has an additional structural particle at the center of each face.

Unit Cells In Cubic Crystal Structures



(a)

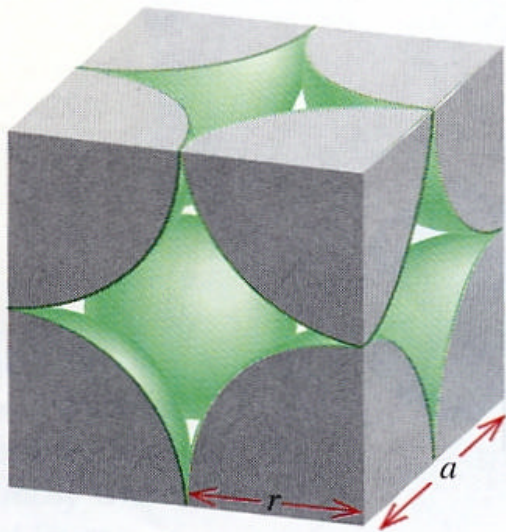
(b)

(c)

simple cubic
(primitive cubic)

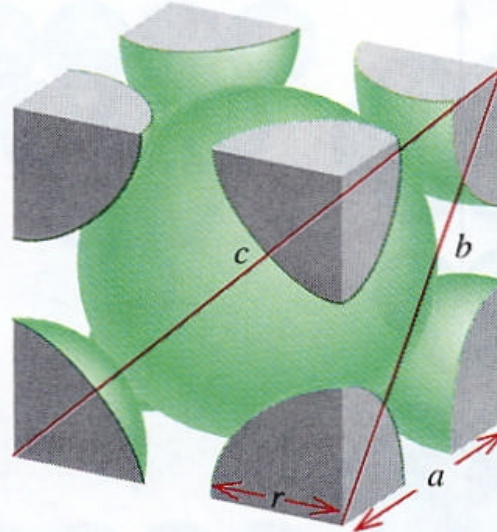
bcc

fcc



scc

$$a = 2r$$



bcc

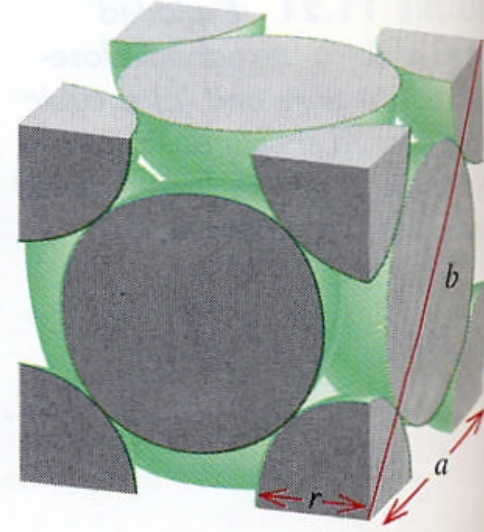
$$b^2 = a^2 + a^2$$

$$c^2 = a^2 + b^2$$

$$= 3a^2$$

$$c = \sqrt{3}a = 4r$$

$$a = \frac{4r}{\sqrt{3}}$$



fcc

$$b = 4r$$

$$b^2 = a^2 + a^2$$

$$16r^2 = 2a^2$$

$$a = \sqrt{8}r$$

FIGURE 11.22 The relationship between the edge length (a) and radius (r) of atoms in the simple cubic cell, body-centered cubic cell, and face-centered cubic cell.

Primitive cubic

Body-centered cubic

Face-centered cubic

Occupancies per Unit Cells

Primitive cubic: $a = 2r$

1 atom/unit cell

$$\begin{aligned}\text{occupancy} &= [4/3(\pi r^3)]/a^3 = [4/3(\pi r^3)]/(2r)^3 \\ &= 0.52 = \mathbf{52\%}\end{aligned}$$

Body-centered cubic: $a = 4r/(3)^{1/2}$

2 atom/unit cell

$$\begin{aligned}\text{occupancy} &= 2 \times [4/3(\pi r^3)]/a^3 = 2 \times [4/3(\pi r^3)]/[4r/(3)^{1/2}]^3 \\ &= 0.68 = \mathbf{68\%}\end{aligned}$$

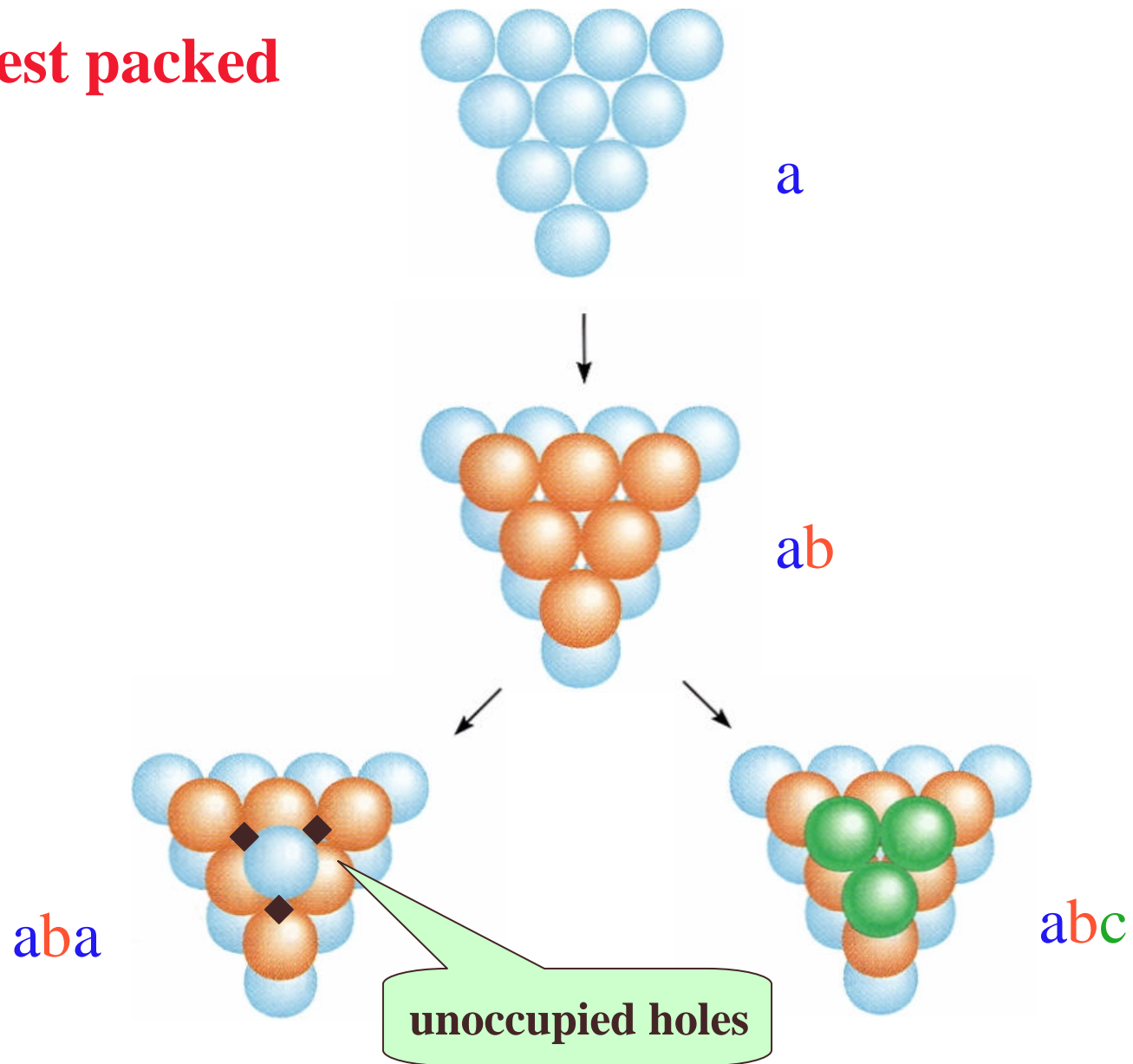
Face-centered cubic: $a = (8)^{1/2} r$

4 atom/unit cell

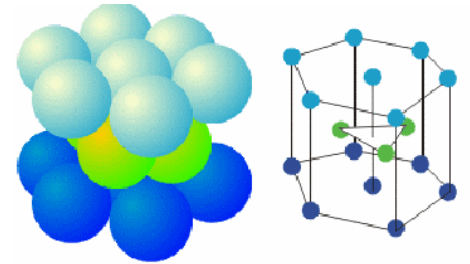
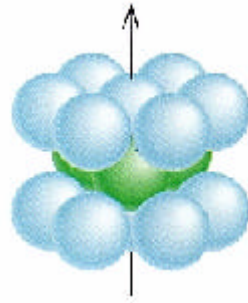
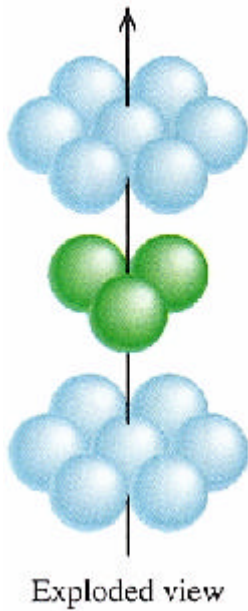
$$\begin{aligned}\text{occupancy} &= 4 \times [4/3(\pi r^3)]/a^3 = 4 \times [4/3(\pi r^3)]/[(8)^{1/2} r]^3 \\ &= 0.74 = \mathbf{74\%}\end{aligned}$$

Closest packed

Closest packed

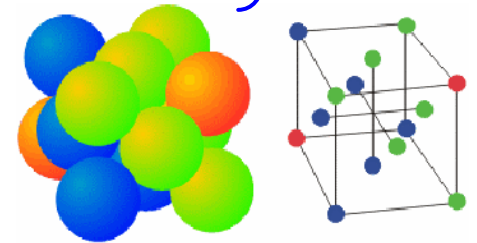
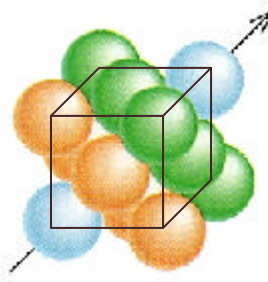
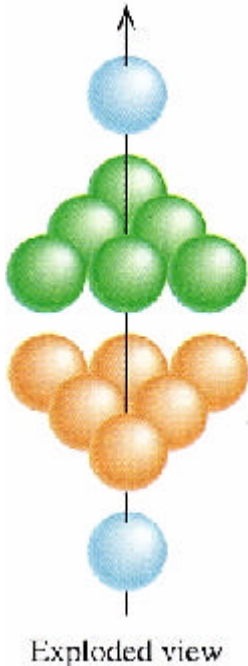


abab



Hexagonal close-packed structure

abcbabc



Cubic close-packed structure

= Face-centered cubic

} polytypes

Crystal Structures of Metals

| | | | | | | | | | | | | | | | |
|---|---|--|---|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|---|----------------|------------------------|
| 3 Li <i>bcc</i> ^b <i>hcp</i> <i>ccp</i> | 4 Be <i>hcp</i> <i>bcc</i> | <i>bcc</i> : body-centered cubic <i>hcp</i> (2 <i>P</i>): hexagonal close-packed <i>ccp</i> (3 <i>P</i>): cubic close-packed 3 <i>P'</i> : distorted <i>ccp</i> 4 <i>P</i> : double hexagonal, length of <i>c</i> axis is doubled 9 <i>P</i> : <i>ABABCBCAC</i> . . . sequence 3·2 <i>PT</i> : diamond structure | | | | | | | | | | 13 Al <i>ccp</i> | 14 Si 3·2 <i>PT</i> | | |
| 11 Na <i>bcc</i> <i>hcp</i> | 12 Mg <i>hcp</i> | 19 K <i>bcc</i> | 20 Ca <i>ccp</i> <i>hcp</i> | 21 Sc <i>hcp</i> <i>bcc</i> | 22 Ti <i>hcp</i> <i>bcc</i> | 23 V <i>bcc</i> | 24 Cr <i>bcc</i> | 25 Mn 3 <i>P'</i> | 26 Fe <i>bcc</i> <i>ccp</i> | 27 Co <i>hcp</i> <i>ccp</i> | 28 Ni <i>ccp</i> | 29 Cu <i>ccp</i> | 30 Zn <i>hcp</i> | 31 Ga other | 32 Ge 3·2 <i>PT</i> |
| 37 Rb <i>bcc</i> | 38 Sr <i>ccp</i> <i>hcp</i> | 39 Y <i>hcp</i> <i>bcc</i> | 40 Zr <i>hcp</i> <i>bcc</i> | 41 Nb <i>bcc</i> | 42 Mo <i>bcc</i> | 43 Tc <i>hcp</i> | 44 Ru <i>hcp</i> | 45 Rh <i>ccp</i> | 46 Pd <i>ccp</i> | 47 Ag <i>ccp</i> | 48 Cd <i>hcp</i> | 49 In 3 <i>P'</i> | 50 Sn 3·2 <i>PT</i> | | |
| 55 Cs <i>bcc</i> | 56 Ba <i>bcc</i> | 71 Lu <i>hcp</i> <i>bcc</i> | 72 Hf <i>hcp</i> <i>bcc</i> | 73 Ta <i>bcc</i> | 74 W <i>bcc</i> | 75 Re <i>hcp</i> | 76 Os <i>hcp</i> | 77 Ir <i>ccp</i> | 78 Pt <i>ccp</i> | 79 Au <i>ccp</i> | 80 Hg other | 81 Tl <i>hcp</i> <i>bcc</i> | 82 Pb <i>ccp</i> | | |
| 57 La 4 <i>P</i> <i>hcp</i> <i>bcc</i> | 58 Ce <i>ccp</i> 4 <i>P</i> <i>bcc</i> | 59 Pr 4 <i>P</i> <i>hcp</i> <i>ccp</i> | 60 Nd 4 <i>P</i> <i>ccp</i> <i>bcc</i> | 61 Pm 4 <i>P</i> | 62 Sm 9 <i>P</i> <i>bcc</i> | 63 Eu <i>bcc</i> | 64 Gd <i>hcp</i> <i>bcc</i> | 65 Tb <i>hcp</i> <i>bcc</i> | 66 Dy <i>hcp</i> <i>bcc</i> | 67 Ho <i>hcp</i> <i>bcc</i> | 68 Er <i>hcp</i> <i>bcc</i> | 69 Tm <i>hcp</i> <i>bcc</i> | 70 Yb <i>ccp</i> <i>bcc</i> <i>hcp</i> | | |
| 89 Ac <i>ccp</i> | 90 Th <i>ccp</i> <i>bcc</i> | 91 Pa <i>bcc</i> <i>ccp</i> | 92 U other <i>bcc</i> | 93 Np other <i>bcc</i> | 94 Pu other <i>bcc</i> | 95 Am 4 <i>P</i> <i>ccp</i> | 96 Cm 4 <i>P</i> <i>ccp</i> | 97 Bk 4 <i>P</i> <i>ccp</i> | 98 Cf | 99 Es | 100 Fm | 101 Md | 102 No | | |

^a Adapted from S. -M. Ho and B. E. Douglas, *J. Chem. Educ.* **1972**, 49, 74.

^b Room-temperature structures are listed first.

Interionic Forces of Attraction



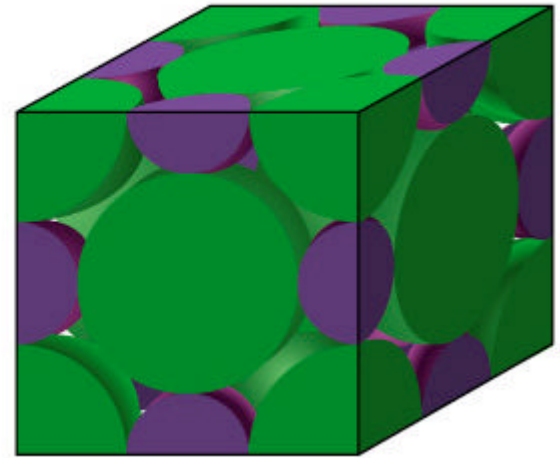
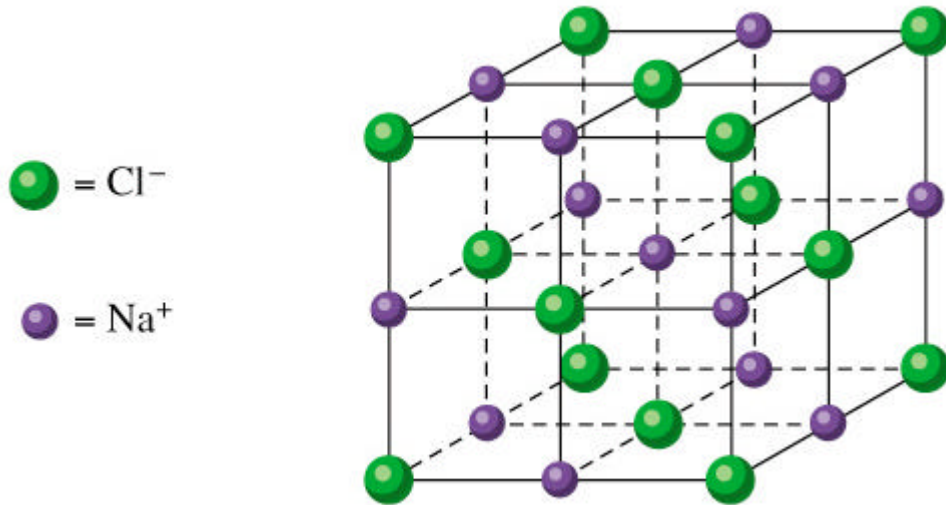
$$E = (Z^+Z^-e^2)/4\pi\epsilon r \quad e = 1.6 \times 10^{-19} \text{ C}$$

In vacuum, $\epsilon_0 = 8.85 \times 10^{-12} \text{ C}^2\text{m}^{-1}\text{J}^{-1}$

In water, $\epsilon_{\text{H}_2\text{O}} = 7.25 \times 10^{-10} \text{ C}^2\text{m}^{-1}\text{J}^{-1} = 82 \epsilon_0$

In liquid ammonia, $\epsilon_{\text{NH}_3} = 2.2 \times 10^{-10} \text{ C}^2\text{m}^{-1}\text{J}^{-1} = 25 \epsilon_0$

Unit Cell of Rock-Salt (Sodium Chloride)



Coord. #: Na^+ : 6; Cl^- : 6

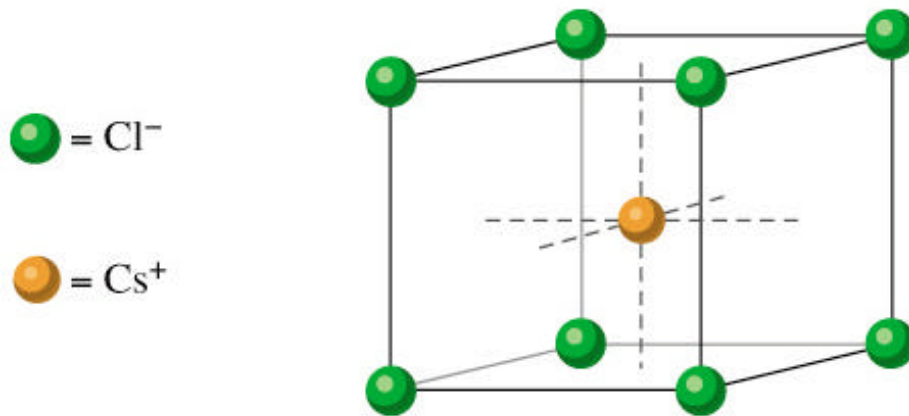
atom/ unit cell

$\text{Na} : \text{Cl} = 4 : 4 = 1 : 1 \Rightarrow \text{NaCl}$

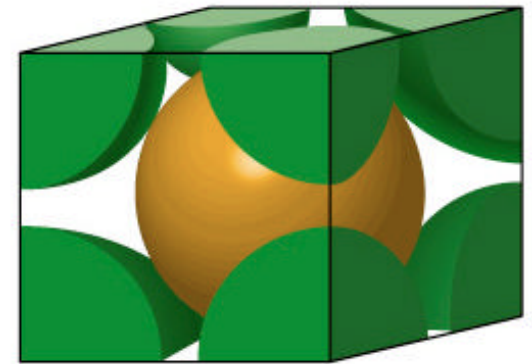
Cl^- at fcc

Na^+ at O_h holes

Unit Cell of Cesium Chloride

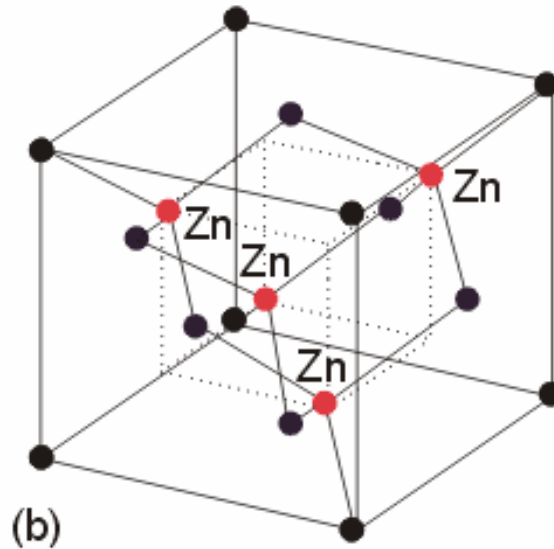
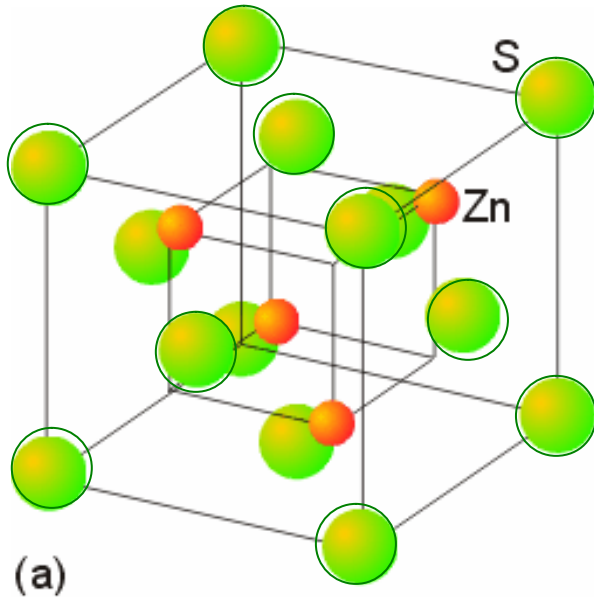


Coord. #: Cs^+ : 8; Cl^- : 8
atom/ unit cell
 $\text{Cs} : \text{Cl} = 1 : 1 \Rightarrow \text{CsCl}$



Cl^- at primitive cubic
 Cs^+ at Cubic holes

Unit Cell of Cubic Zinc Sulfide (Sphalerite or Zinc blende)

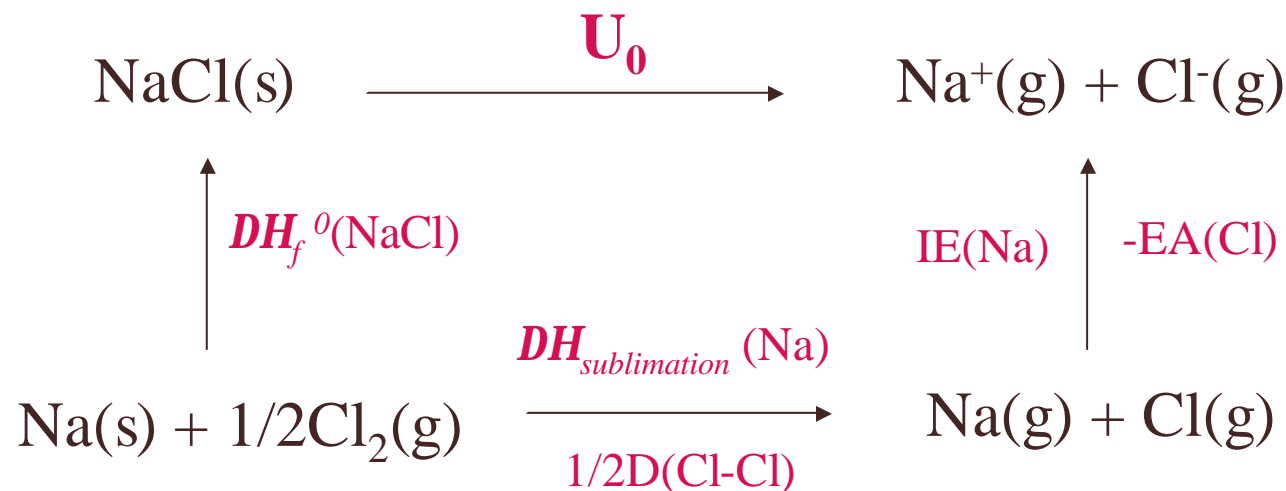


Coord. #: Zn^{2+} : 4; S^{2-} : 4
atom/ unit cell

$\text{Zn} : \text{S} = 4 : 4 = 1 : 1 \Rightarrow \text{ZnS}$

S^{2-} at fcc
 Zn^{2+} at $\frac{1}{2}$ Td holes

A Born-Haber Cycle to Calculate Lattice Energy

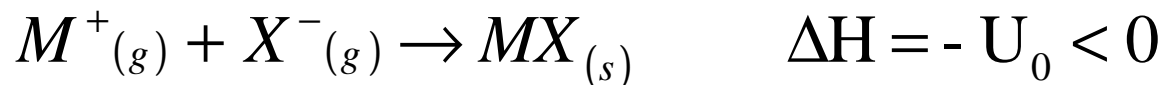


$$\text{lattice energy } U_0 = -DH_f^0(\text{NaCl}) + DH_{\text{sublimation}}(\text{Na}) + 1/2D(\text{Cl-Cl}) + \text{IE}(\text{Na}) - \text{EA}(\text{Cl})$$

$$= (+411 + 107 + 122 + 496 - 349) \text{ kJ/mol}$$

$$= +787 \text{ kJ/mol}$$

Lattice Energy & Madelung Constant



U_0 : lattice energy

Factors contributed to Lattice energy

- *electrostatic energy* ~90%
 - *repulsion of close shells* ~8%
 - *dispersion forces* ~1%
 - *zero-point energy (lattice vibration at 0K)*
 - *correction for heat capacity*
- } ~1%

Electrostatic energy in a crystal lattice, between a pair of ions

$$E_c = \frac{A(Z^+ Z^- e^2)}{4\pi\epsilon_0 r}$$

A : Madelung Constant

For NaCl crystal, $Z^+ = Z^- = 1$
 $r = d$

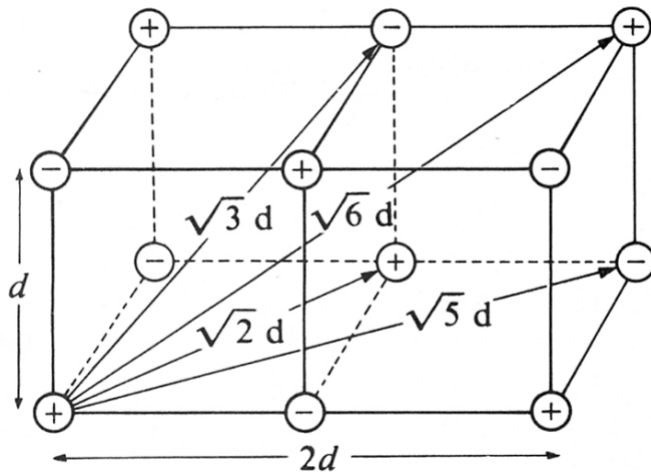


Figure 5.22 Distances to neighboring ions in the NaCl lattice.

$$\begin{aligned}
 E_c &= -\frac{6e^2}{d} + \frac{12e^2}{\sqrt{2}d} - \frac{8e^2}{\sqrt{3}d} + \frac{6e^2}{2d} - \frac{24e^2}{\sqrt{5}d} + \frac{24e^2}{\sqrt{6}d} \dots \\
 &= -\frac{e^2}{d} \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} \dots \right)
 \end{aligned}$$

$$A = 6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \frac{24}{\sqrt{5}} - \frac{24}{\sqrt{6}} \dots$$

The value of Madelung constant is determined only by the “geometry of the lattice”, and independent of the “ionic radius” and “charge”.

Table 5.12 Values of Madelung constants^a

| <i>Structure</i> | <i>Madelung constant</i> | <i>Structure</i> | <i>Madelung constant</i> |
|------------------------------|--------------------------|--|--------------------------|
| Sodium chloride | 1.74756 | Rutile (TiO ₂) | 2.408 |
| Cesium chloride | 1.76267 | Anatase (TiO ₂) | 2.400 |
| Zinc blende (ZnS) | 1.63806 | Cadmium iodide | 2.36 |
| Wurtzite (ZnS) | 1.64132 | β-Quartz (SiO ₂) | 2.201 |
| Fluorite (CaF ₂) | 2.51939 | Corundum (Al ₂ O ₃) | 4.040 |

^a Values are geometrical Madelung constants. “Conventional” values differ in cases where the charges differ for the cations and anions, as for CaF₂, TiO₂, and Al₂O₃.

Born equation

$$\text{PE} = \frac{Ae^2 Z_1 Z_2}{d} + \frac{Be^2}{d^n}$$

electrostatic energy

repulsion of close shells

B: constant

n: Born exponent

| Ion configuration | <i>n</i> |
|---------------------|----------|
| He | 5 |
| Ne | 7 |
| Ar, Cu ⁺ | 9 |
| Kr, Ag ⁺ | 10 |
| Xe, Au ⁺ | 12 |

At minimum PE, attractive and repulsive forces are balanced, and $d = d_0$.

$$\frac{\partial(PE)}{\partial d} = 0$$

$$d_0 = \left(-\frac{nB}{AZ_1Z_2} \right)^{1/(n-1)}$$

$$B = \frac{-d_0^{(n-1)}AZ_1Z_2}{n}$$

$$(PE)_0 = \frac{-Ae^2Z_1Z_2}{d_0} \left(\frac{1}{n} - 1 \right)$$

Let $U_0 = -(PE)_0 N$ N : Avogadro's number

$$U_0 = \frac{-NAe^2Z_1Z_2}{d_0} \left(1 - \frac{1}{n} \right) \quad \text{Born-Lande equation}$$

$$U_0 = \frac{-NAe^2 Z_1 Z_2}{d_0} \left(1 - \frac{1}{n} \right)$$

For NaCl

$$A = 1.74756$$

$$Z_1 = 1, Z_2 = -1$$

$$d_0 = r_{Na^+} + r_{Cl^-} = 2.81 \times 10^{-10} \text{ m}$$

$$n = (n_{Na^+} + n_{Cl^-}) / 2 = (7+9)/2 = 8$$

$$\Rightarrow U_0 = 755.2 \text{ kJ/mol}$$

experimental $U_0 = 770 \text{ kJ/mol}$

Modification of Born-Lande equation

1. Born-Mayer equation

Improving the repulsion

$$U_0 = \frac{NAZ^+Z^-e^2}{4\pi\epsilon_0d_0} \left(1 - \frac{0.345}{d_0}\right)$$

Unit in ? , 10^{-10} m

2. Kapustinskii equation

A ? crystal lattice ? r_+/r_- ? r_0

$$U_0 = \frac{-nkZ^+Z^-}{d_0} \left(1 - \frac{0.345}{d_0}\right)$$

A/n ~constant

$$k = 1.21 \text{ MJ. ? mol}^{-1}$$

n = ions per formula

e.g. $n = 2$ for NaCl

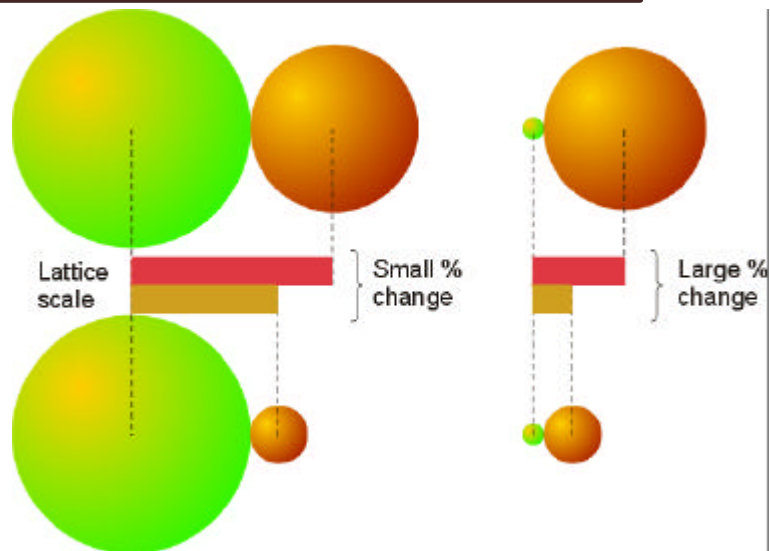
$n = 5$ for Al_2O_3



| Data at 298K | Mg | Ca | Sr | Ba |
|------------------------|--------|--------|--------|--------|
| ΔG^0 (kJ/mol) | +48.3 | +130.4 | +183.8 | +218.1 |
| ΔH^0 (kJ/mol) | +100.6 | +178.3 | +234.6 | +269.3 |
| ΔS^0 (J/K mol) | +175.0 | +160.6 | +171.0 | +172.1 |
| T (°C) | 300 | 840 | 1100 | 1300 |

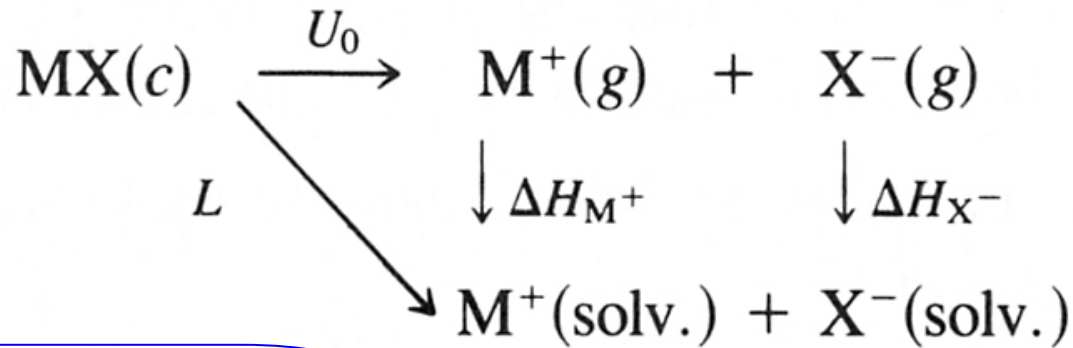
$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\text{decomposition } T = \frac{\Delta H^0}{\Delta S^0}$$



A small cation increases the lattice enthalpy of the oxide more than that of a carbonate.

Solubility of ionic compounds



Enthalpy of solution

Hydration enthalpy

$$L = \underbrace{\Delta H_{\text{M}^+} + \Delta H_{\text{X}^-}}_{< 0} + \underbrace{U_0}_{> 0}$$

Free energy of solution

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = L - T\Delta S^0$$

$$RT \ln K_{\text{sp}} = -L + T\Delta S^0$$

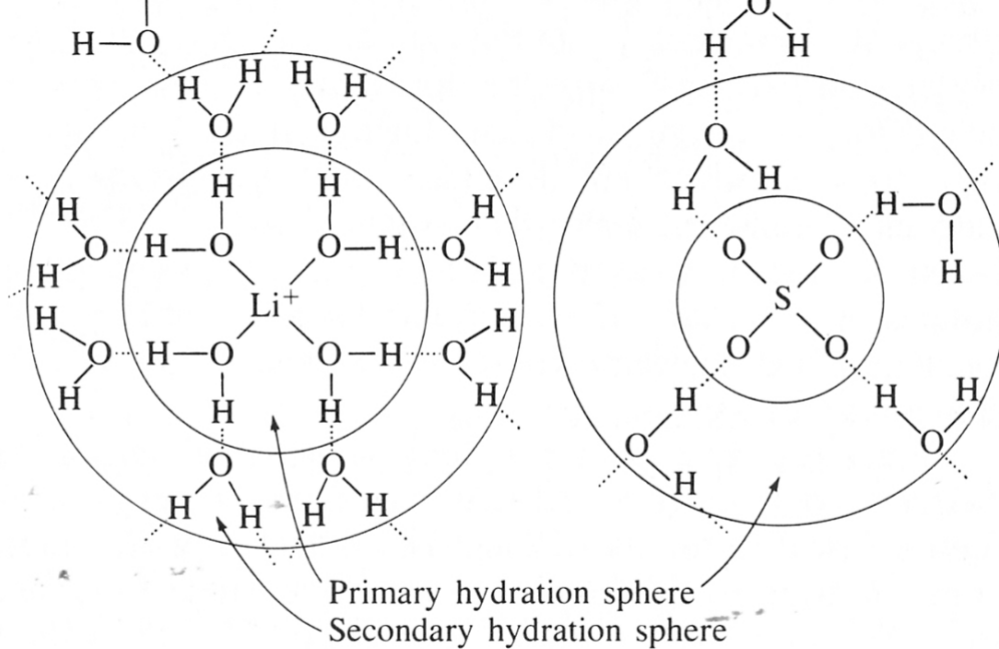


Figure 5.23 Hydrated Li^+ and SO_4^{2-} ions.

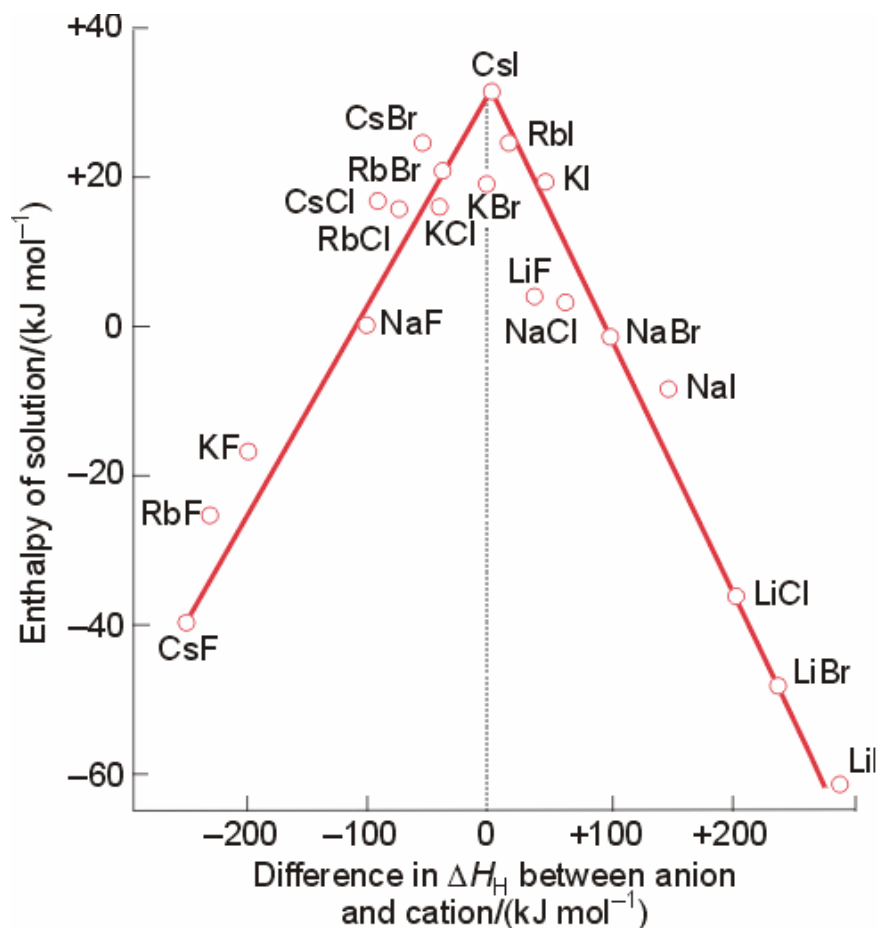
Hydration enthalpy

$$\Delta H_{\text{hyd}} = -\frac{Z^2}{2r} \left(1 - \frac{1}{e} \right)$$

$$U_0 \propto \frac{1}{r_+ + r_-}$$

$$\Delta H_{\text{hydration}} = \Delta H_{M^+} + \Delta H_{X^-} = \infty \frac{1}{r_+} + \frac{1}{r_-}$$

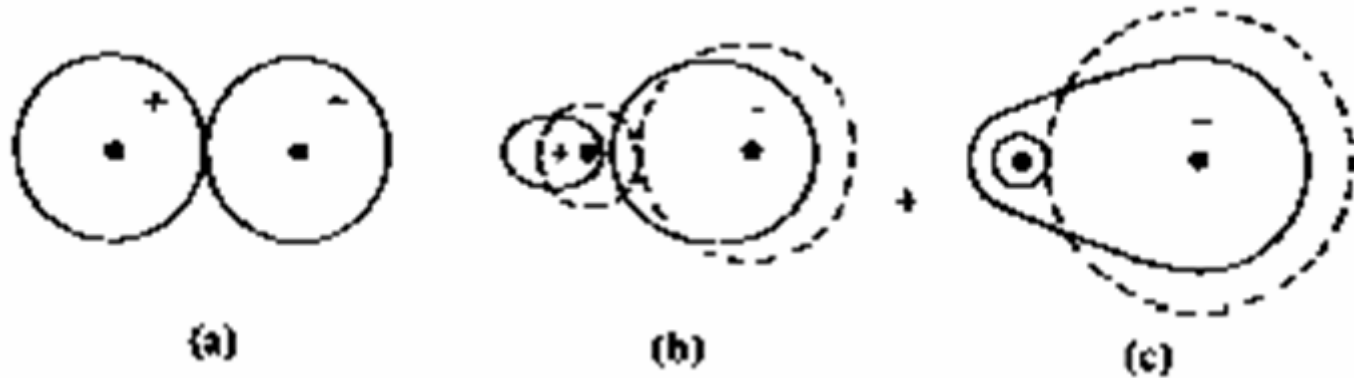
- In general, difference in ionic size favors solubility in water.
- Ionic compound MX tends to be most soluble when $r_X - r_M > 0.8$?



Correlation between $\Delta H_{\text{solution}}$ and the differences between the hydration enthalpy of the ions

Fajan's rules

Fajan's Rule: the degree of covalent character of ionic bond



Polarization effects: (a) idealized ion pair with no polarization; (b) mutually polarized ion pair; (c) polarization sufficient to form covalent bond. Dashed lines represent hypothetical unpolarized ions.

In 1923, Fajan suggested rules to predict the degree of covalent character in ionic compounds:

The **polarization of an ionic bond** and thus **the degree of covalency is high** if :

1) the charges on the ions are high.

eg., Al^{3+} ; Ti^{4+} ----- favors covalent character.

Na^{+} ; K^{+} ----- favors ionic character.

2) the cation is small.

e.g., Na^{+} ion is larger than that of Al^{3+}

Thus, Al^{3+} favors covalent character.

3) the anion is large.

e.g. F^{-} ionic radius : 0.136 nm favors ionic character.

I^{-} ionic radius : 0.216 nm favors covalent character.

4) An incomplete valence shell electron configuration

Noble gas configuration of the cation better shielding and less polarizing power

e.g. Hg^{2+} ($r = 102 \text{ pm}$) is more polarizing than Ca^{2+} ($r = 100 \text{ pm}$)

{ HgO decomposed at 500°C
 CaO m.p. 2613°C

| Halides | m.p. ($^\circ\text{C}$) | Crys str | Halides | m.p. ($^\circ\text{C}$) | Crys str |
|-----------------|---------------------------|--------------|-----------------|---------------------------|-----------|
| HgF_2 | 645 (dec) | cubic | CaF_2 | 1418 | cubic |
| HgCl_2 | 276 | orthorhombic | CaCl_2 | 775 | cubic |
| HgBr_2 | 236 | rhombohedral | CaBr_2 | 742 | rhomb. |
| HgI_2 | 259 | tetragonal | CaI_2 | 783 | hexagonal |

Examples:

For ions with noble gas ($ns^2 np^6$) structure, the only factors that have to be considered are size and charge factor.

a) Charge factor

i) Cations



Increasing charge : increase in polarizing power

ii) Anions



Increase in ionic charge, more ready to be polarized

covalency

| Chlorides | melting point / °C | boiling point / °C | Conductance in molten state |
|-------------------|-----------------------|-----------------------|--------------------------------|
| NaCl | 800 | 1440 | 133 |
| MgCl ₂ | 715 | 1410 | 29 |
| AlCl ₃ | sublimation | 183 | 1.5×10^{-5} |
| SiCl ₄ | -70 | 57 | |

AlCl₃ has covalent character. In fact, AlCl₃ exists as dimer Al₂Cl₆ at room conditions.

b) Size factor

i) Cations



The smaller the cation, the higher is its polarizing power

| Chlorides | melting point / °C | Conductance in molten state |
|-----------------|--------------------|-----------------------------|
| BeCl_2 | 404 | 0.056 |
| MgCl_2 | 715 | 29 |
| CaCl_2 | 774 | 52 |
| SrCl_2 | 870 | 56 |
| BaCl_2 | 955 | |

↑
covalency

ii) Anions



The larger the anion, the more polarizable is the anion.

eg.,

| | NaF | NaCl | NaBr | NaI |
|--------------------|-----|------|------|-----|
| melting point / °C | 990 | 800 | 755 | 651 |

covalency



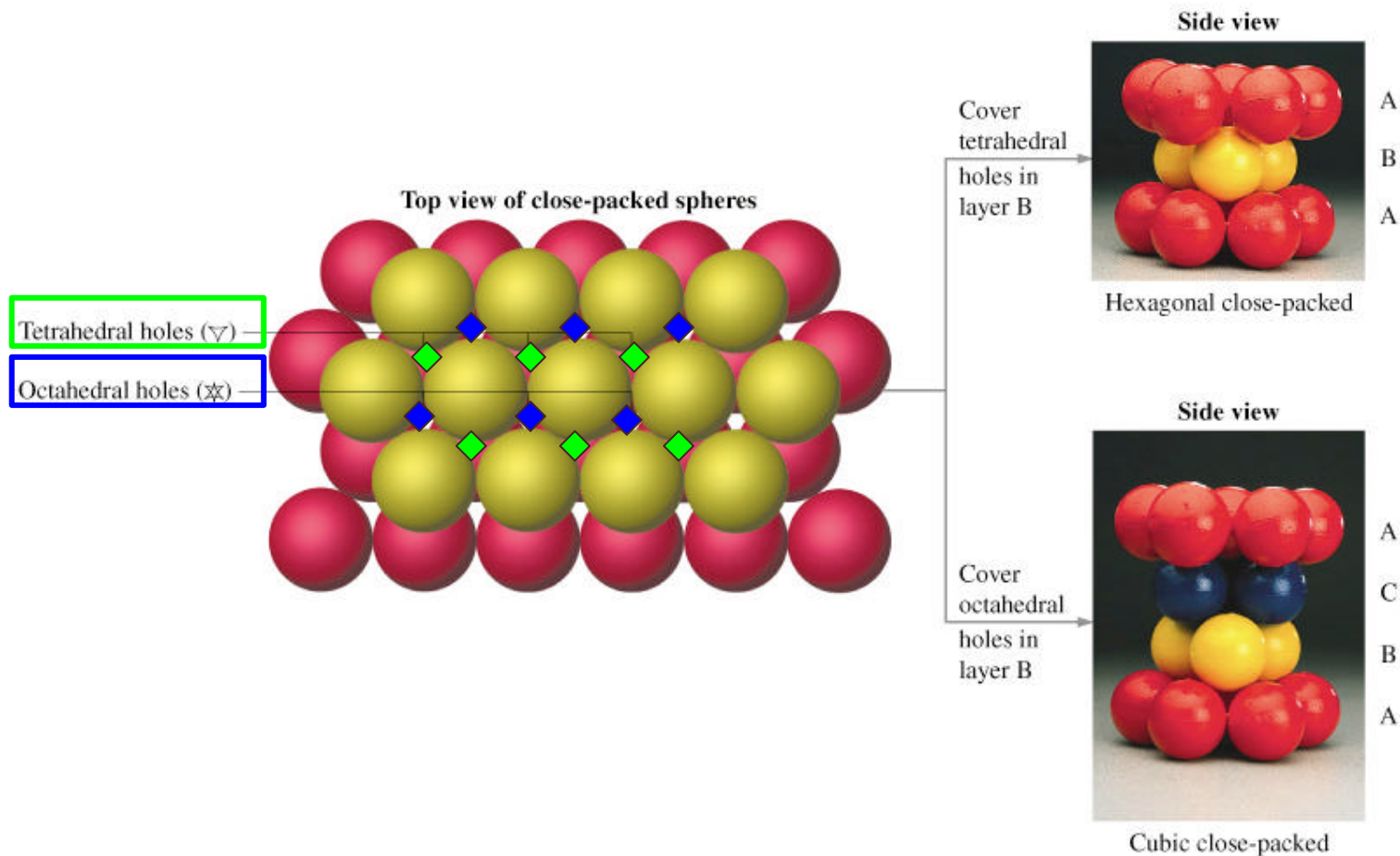
Some covalent character

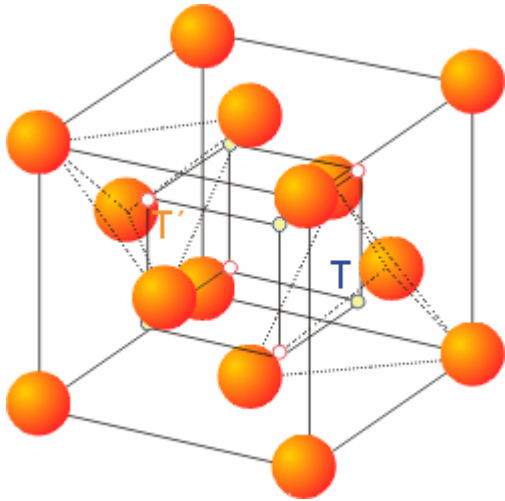
| Carbonates | Decomp. Temp. (°C) | | Oxides | m.p. (°C) |
|-------------------|--------------------|--------------------|--------|-----------|
| BeCO ₃ | 250 | wurtzite structure | BeO | 2530 |
| MgCO ₃ | 540 | NaCl structure | MgO | 2826 |
| CaCO ₃ | 900 | | CaO | 2613 |
| SrCO ₃ | 1289 | | SrO | 2430 |
| BaCO ₃ | 1360 | | BaO | 1923 |

↑ covalency

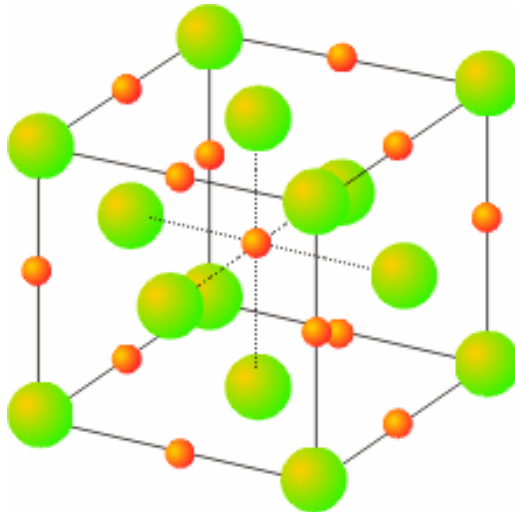
Ionic compounds

Close-packing of Spheres in Three Dimensions

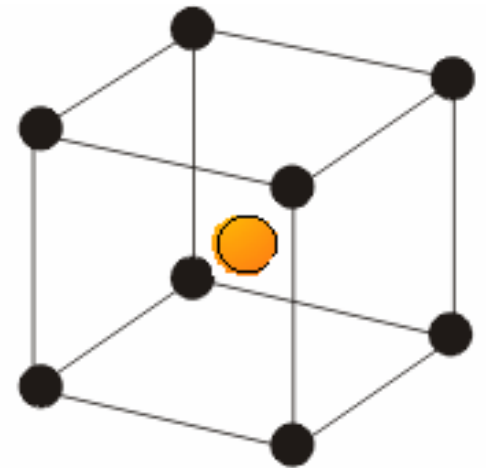




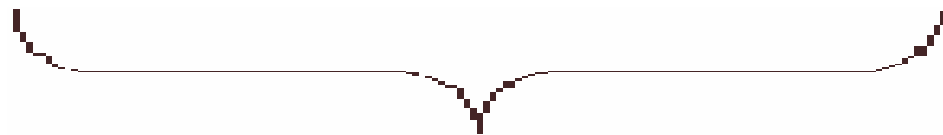
Tetrahedral holes



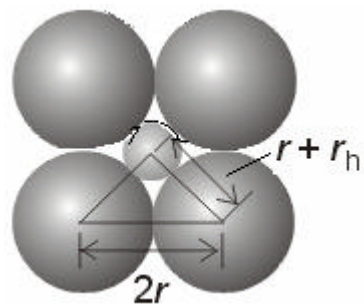
Octahedral holes



Cubic holes



Close packed structure



$$r_h/r = 0.414$$

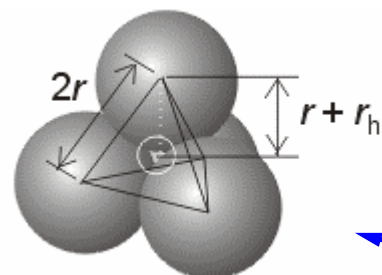
Coordination
number

Radius
ratio

Diagram

8

>0.7



$$r_h/r = 0.225$$

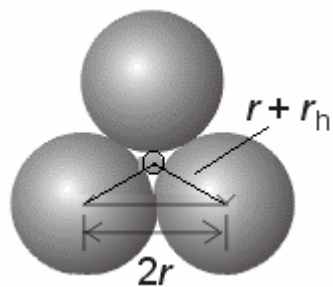
6

0.4–0.7



4

0.2–0.4



$$r_h/r = 0.156$$

3

0.1–0.2



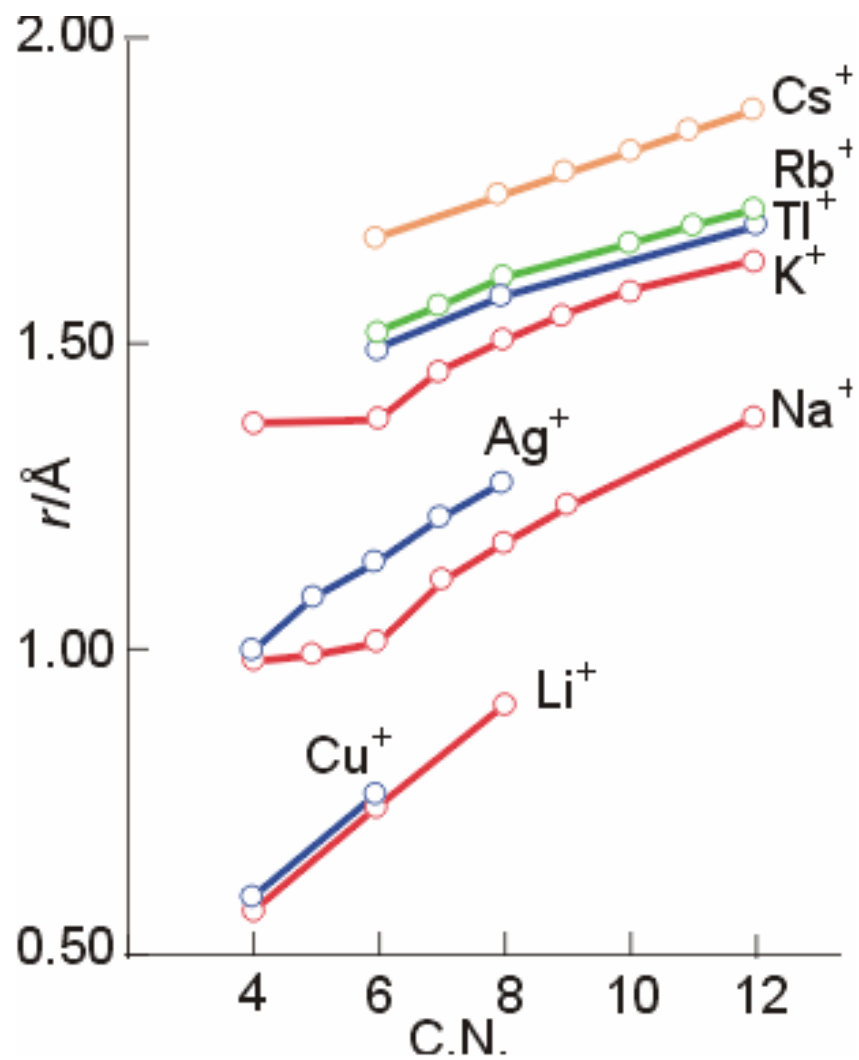
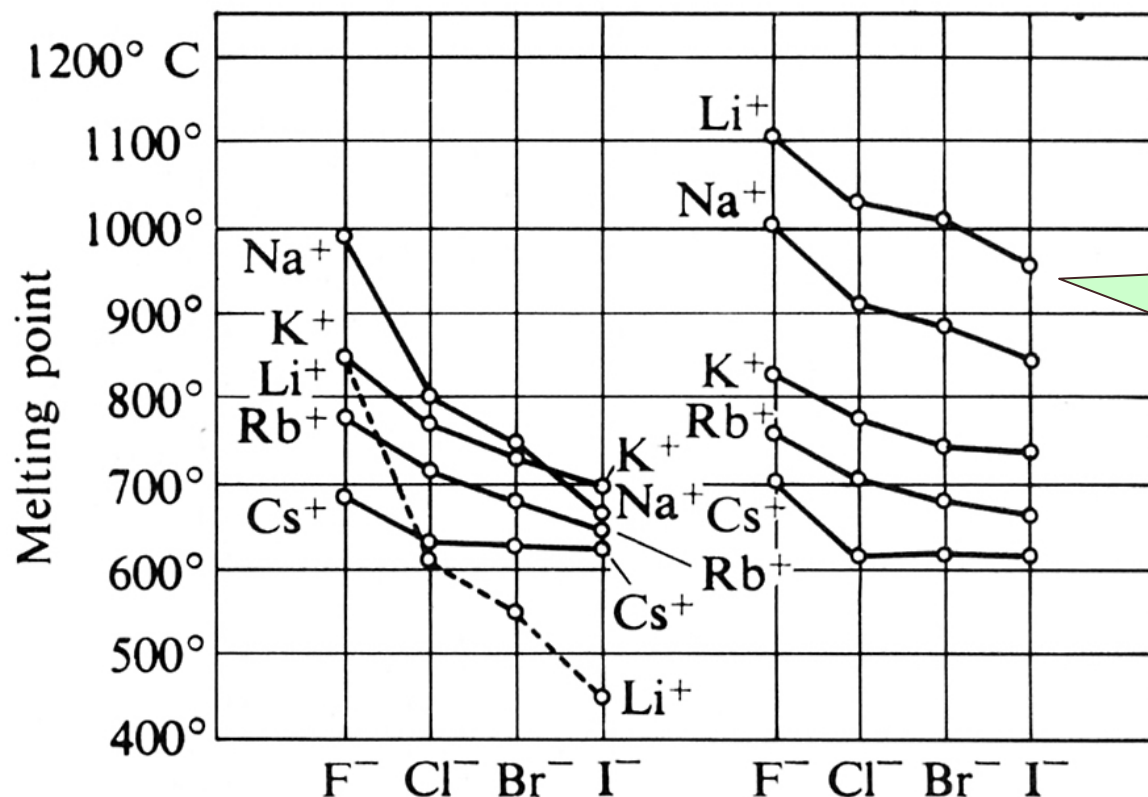


Table 5.4 Radius ratios for arrangements of rigid spheres

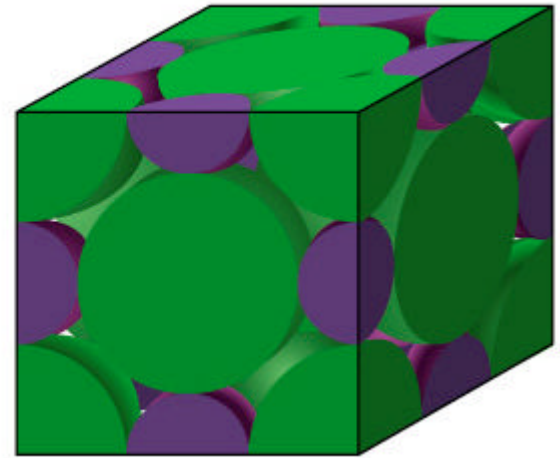
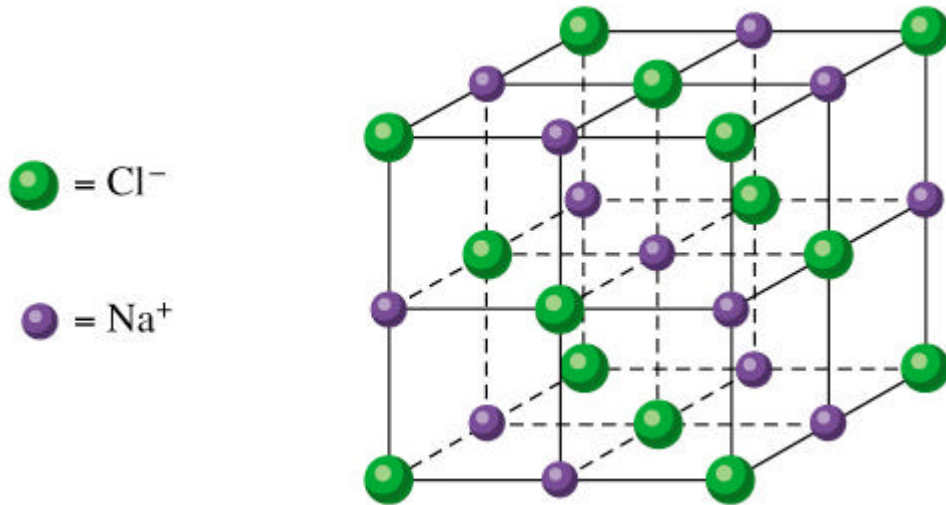
| Coordination number of M | Arrangement of X | Radius ratios | | Crystal structure corresponding to cation C.N. |
|--------------------------------|---------------------|------------------|-------------------|--|
| | | $\rho = r_M/r_X$ | $\rho' = r_X/r_M$ | |
| 3 | Triangular | 0.150–0.225 | 4.44–5.67 | Antifluorite, ZnS |
| 4 | Tetrahedral | 0.225–0.414 | 2.42–4.44 | |
| 4 | Planar | 0.414–0.732 | 1.37–2.42 | |
| 6 | Octahedral | 0.414–0.732 | 1.37–2.42 | NaCl, TiO ₂ , CdCl ₂ |
| 8 | Cubic | 0.732–1.00 | 1.00–1.37 | CsCl, CaF ₂ |



Considering
anion-anion
repulsion

Figure 5.21 The observed melting points of the alkali halides (*left*) and values corrected for the radius-ratio effect (*right*). (Reproduced with permission from Linus Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University, Ithaca, NY. Copyright © 1960 by Cornell University Press.)

Unit Cell of Rock-Salt (Sodium Chloride)



Coord. #: Na^+ : 6; Cl^- : 6

atom/ unit cell

$\text{Na} : \text{Cl} = 4 : 4 = 1 : 1 \Rightarrow \text{NaCl}$

Cl^- at fcc

Na^+ at O_h holes

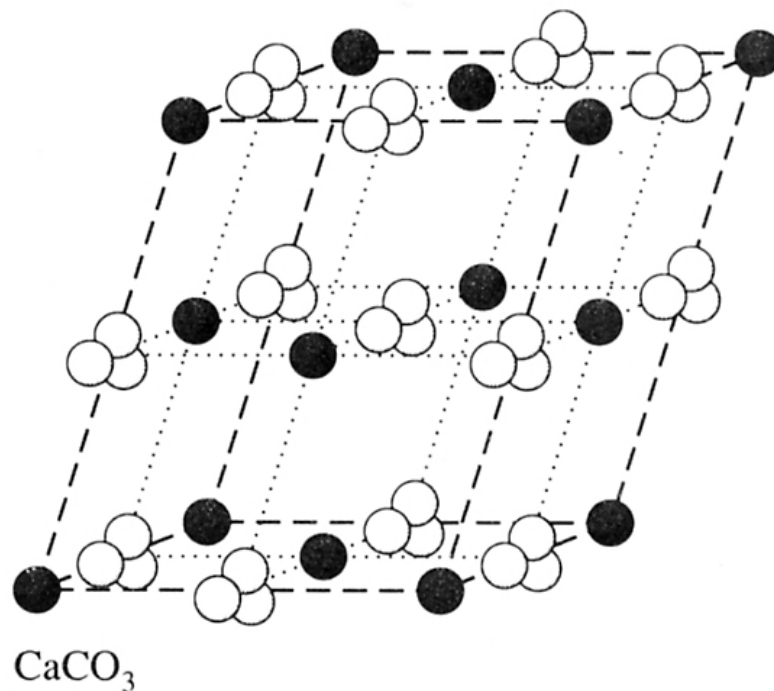
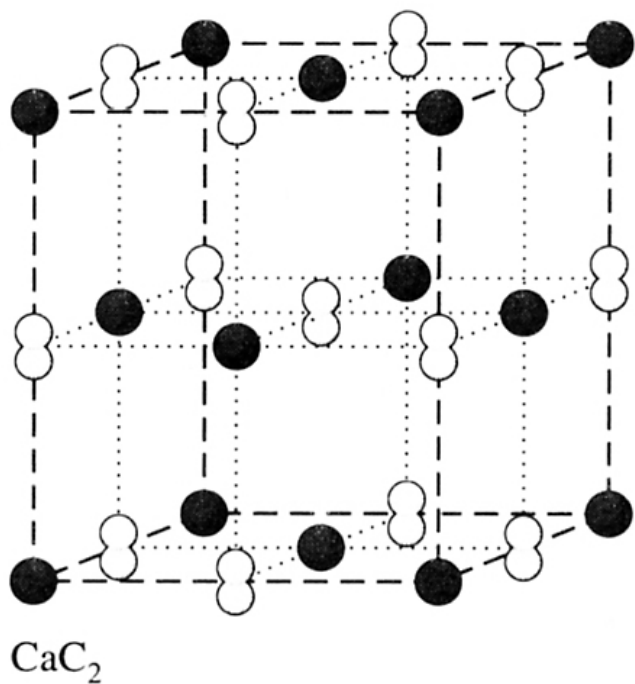
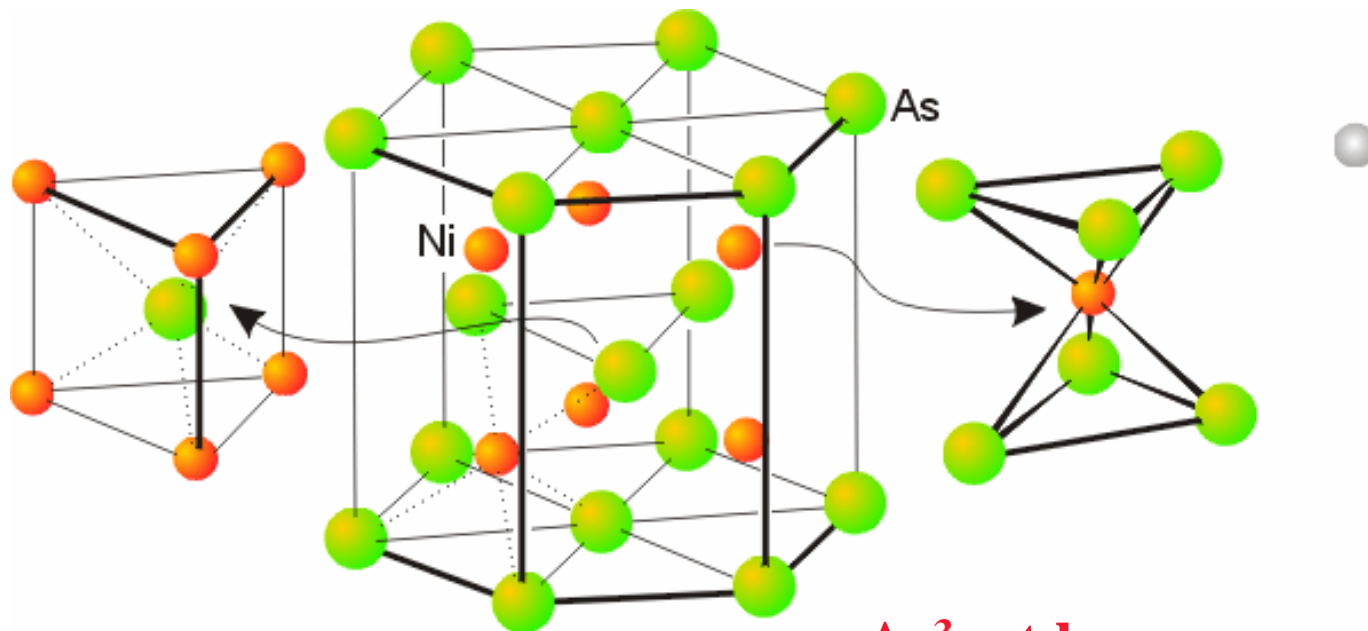


Figure 5.11 Structures of CaC_2 and CaCO_3 . Carbons of CO_3^{2-} are not visible.

Rock-salt structure

Unit Cell of NiAs

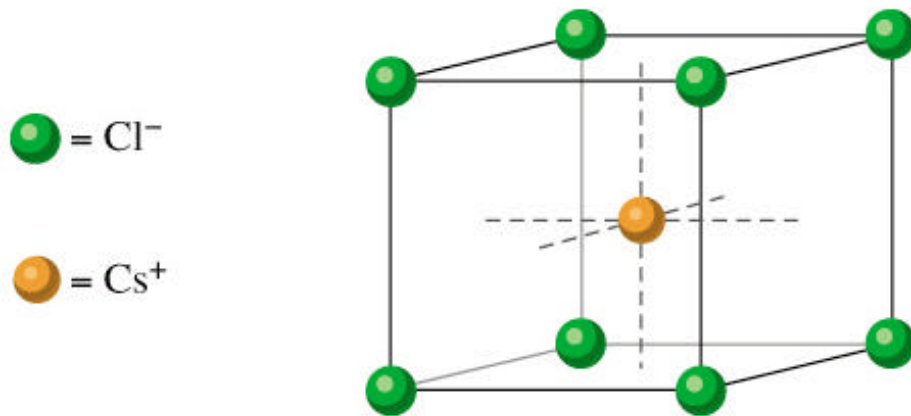


Polarizable cation
& anion

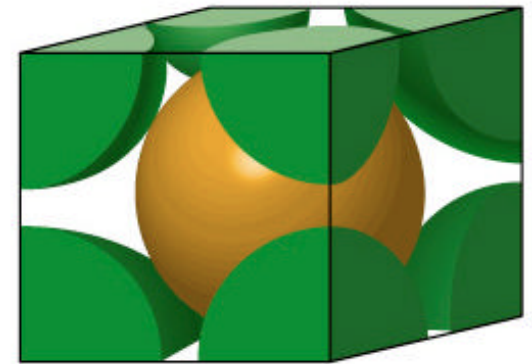
As^{3-} at hcp

Ni^{3+} at O_h holes

Unit Cell of Cesium Chloride

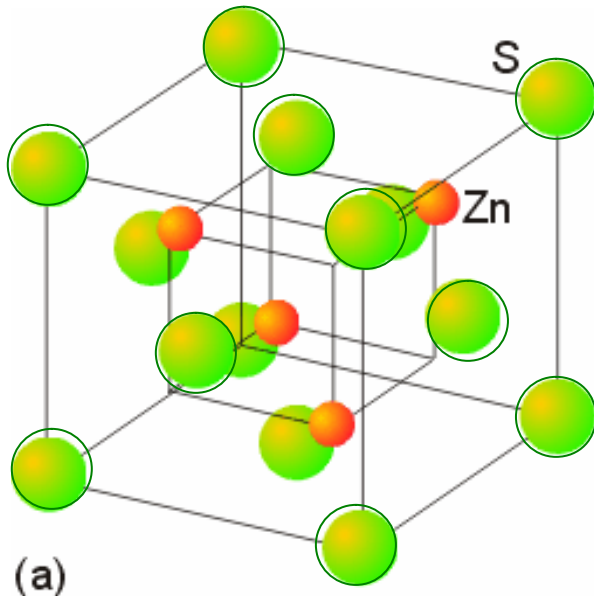


Coord. #: Cs^+ : 8; Cl^- : 8
atom/ unit cell
 $\text{Cs} : \text{Cl} = 1 : 1 \Rightarrow \text{CsCl}$



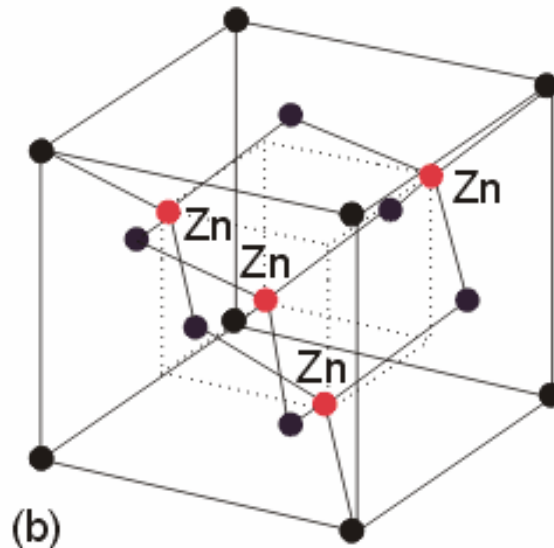
Cl^- at primitive cubic
 Cs^+ at Cubic holes

Unit Cell of Cubic Zinc Sulfide (Sphalerite or Zinc blende)



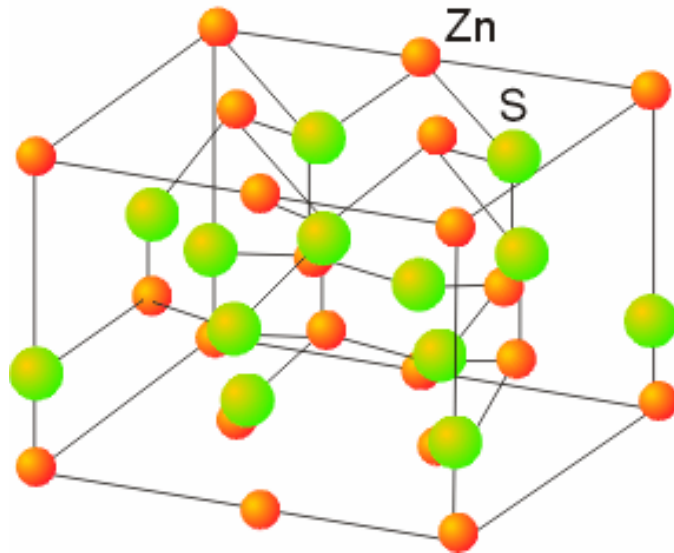
Coord. #: Zn^{2+} : 4; S^{2-} : 4
atom/ unit cell

$\text{Zn} : \text{S} = 4 : 4 = 1 : 1 \Rightarrow \text{ZnS}$

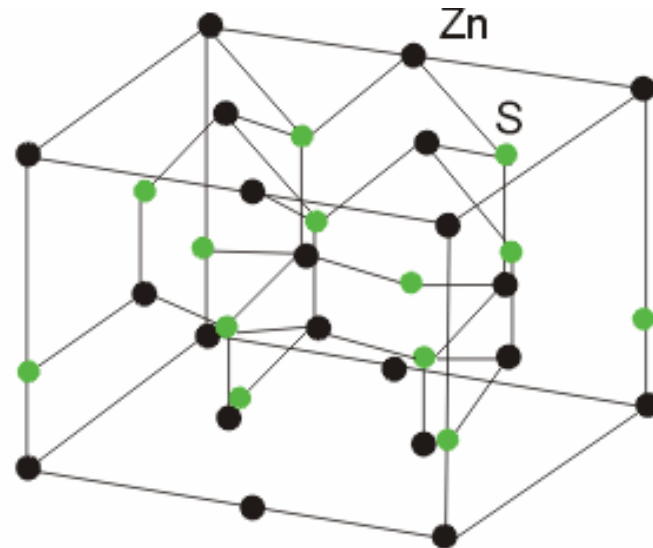


S^{2-} at fcc
 Zn^{2+} at $\frac{1}{2}$ Td holes

Unit Cell of Hexagonal Zinc Sulfide (Wurtzite)



Polymorph of ZnS



S^{2-} at hcp

Zn^{2+} at $\frac{1}{2}$ Td holes

PtS

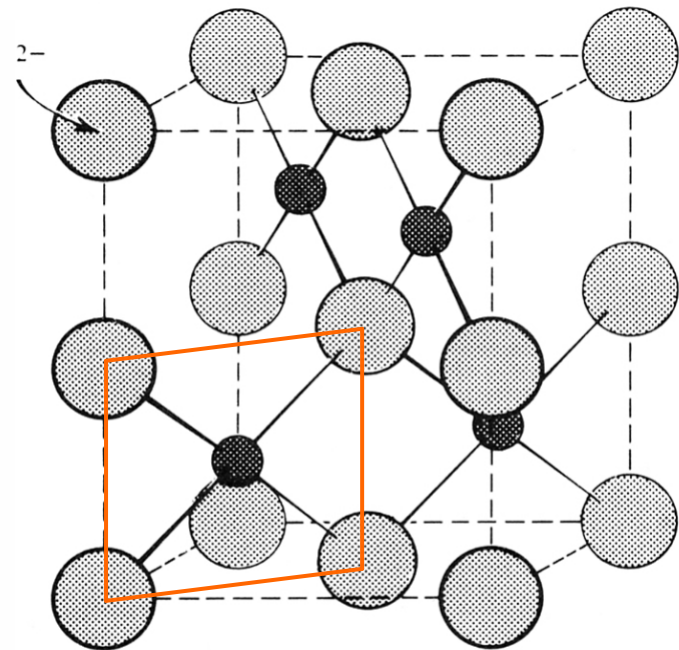
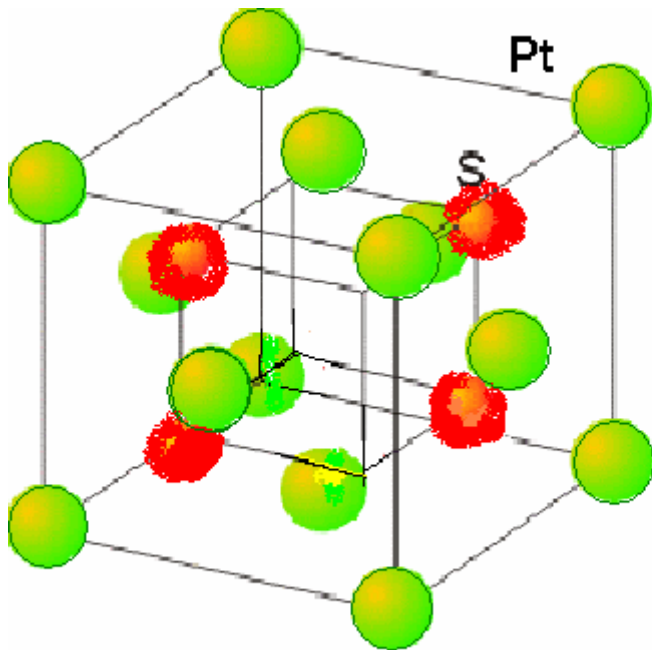


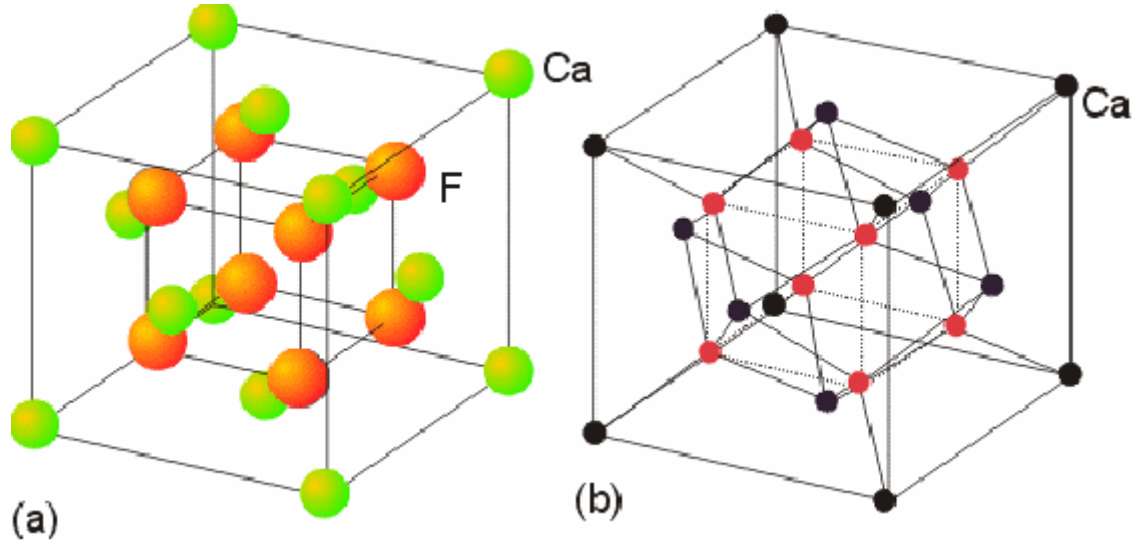
Figure 5.9 The PtS structure showing the planar PtS_4 units. The larger ions are S^{2-} .

Pt^{2+} at fcc

S^{2-} at $\frac{1}{2}$ Td holes

PtS_4 unit is planar \Rightarrow Pt-S more covalent

Unit Cell of Fluorite Structure (Calcium Fluoride)



Coord. #: Ca^{2+} : 8; F^- : 4

atom/ unit cell

$\text{Ca} : \text{F} = 4 : 8 = 1 : 2 \implies \text{CaF}_2$

Ca^{2+} at fcc

F^- at Td holes

- Fluorite Structure- MX_2

Large M

- Antifluorite structure- M_2X

Large X, e.g. Na_2O

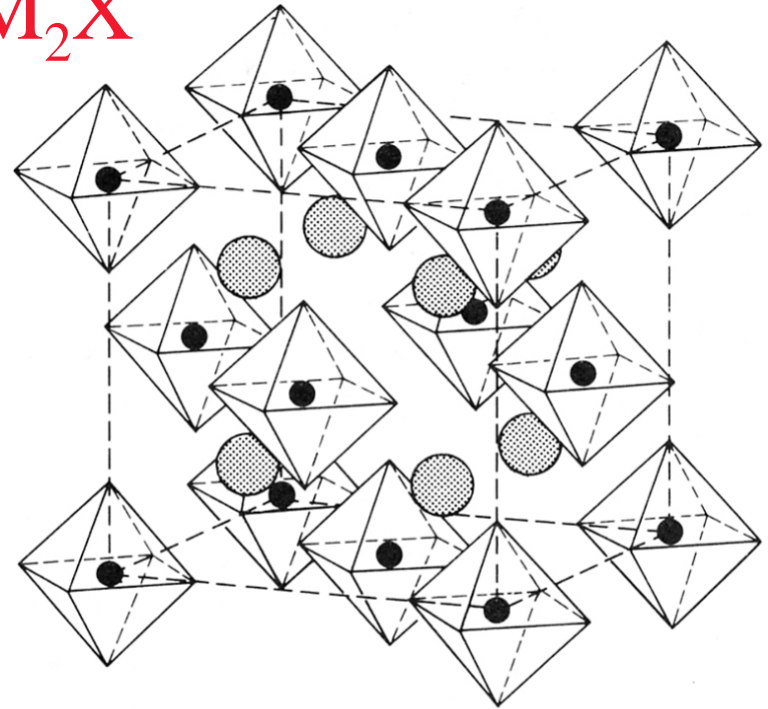
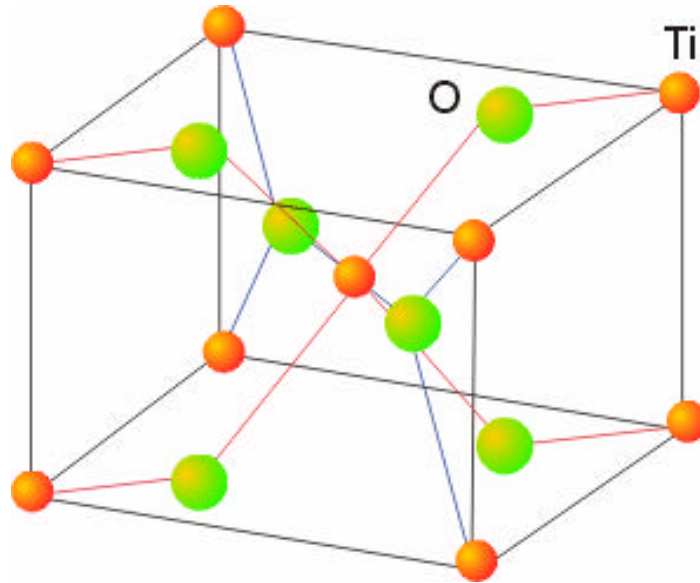


Figure 5.10 The K_2PtCl_6 structure showing the $[\text{PtCl}_6]^{2-}$ octahedra in a *ccp* arrangement with K^+ in tetrahedral sites.

Unit Cell of Rutile TiO_2



Coord. #: Ti: 6; O: 3

atom/ unit cell

Ti: O = 2: 4 = 1: 2

O^{2-} at hcp

Ti^{4+} at $\frac{1}{2} \text{O}_h$ holes

Table 5.5 Structures of some compounds of the type MX

| <i>Ions</i> | <i>Halides</i> | | | | <i>Ions</i> | <i>Oxygen Family</i> | | | |
|-------------|----------------|----------|------|---|-------------|----------------------|----------------|------|------|
| | F | Cl | Br | I | | O | S | Se | Te |
| Li | ← NaCl → | | | | Be | W ^a | Z ^b | Z | Z |
| Na | ← NaCl → | | | | Mg | NaCl | NaCl | NaCl | Z |
| K | ← NaCl → | | | | Ca | NaCl | NaCl | NaCl | NaCl |
| Rb | ← NaCl → | | | | Sr | NaCl | NaCl | NaCl | NaCl |
| Cs | NaCl | ← CsCl → | | | Ba | NaCl | NaCl | NaCl | NaCl |
| Cu | — | Z | Z | Z | Zn | W | W | W | W |
| | | | | | | | Z | Z | Z |
| Ag | NaCl | NaCl | NaCl | W | Cd | NaCl | W | W | Z |
| | | | | | | | Z | | |
| | | | | | Hg | Other ^c | Z | Z | Z |

^aWurtzite. ^bZinc blende. ^cSee page 731.

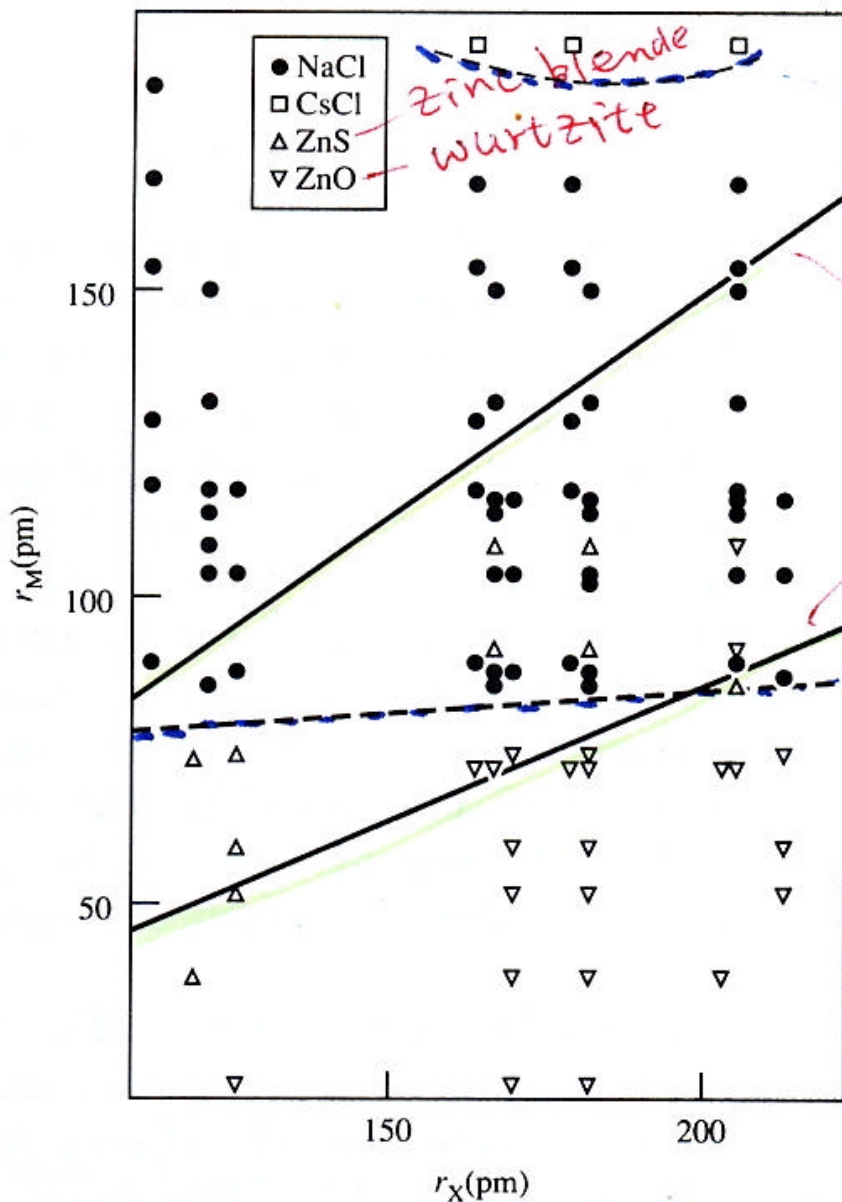
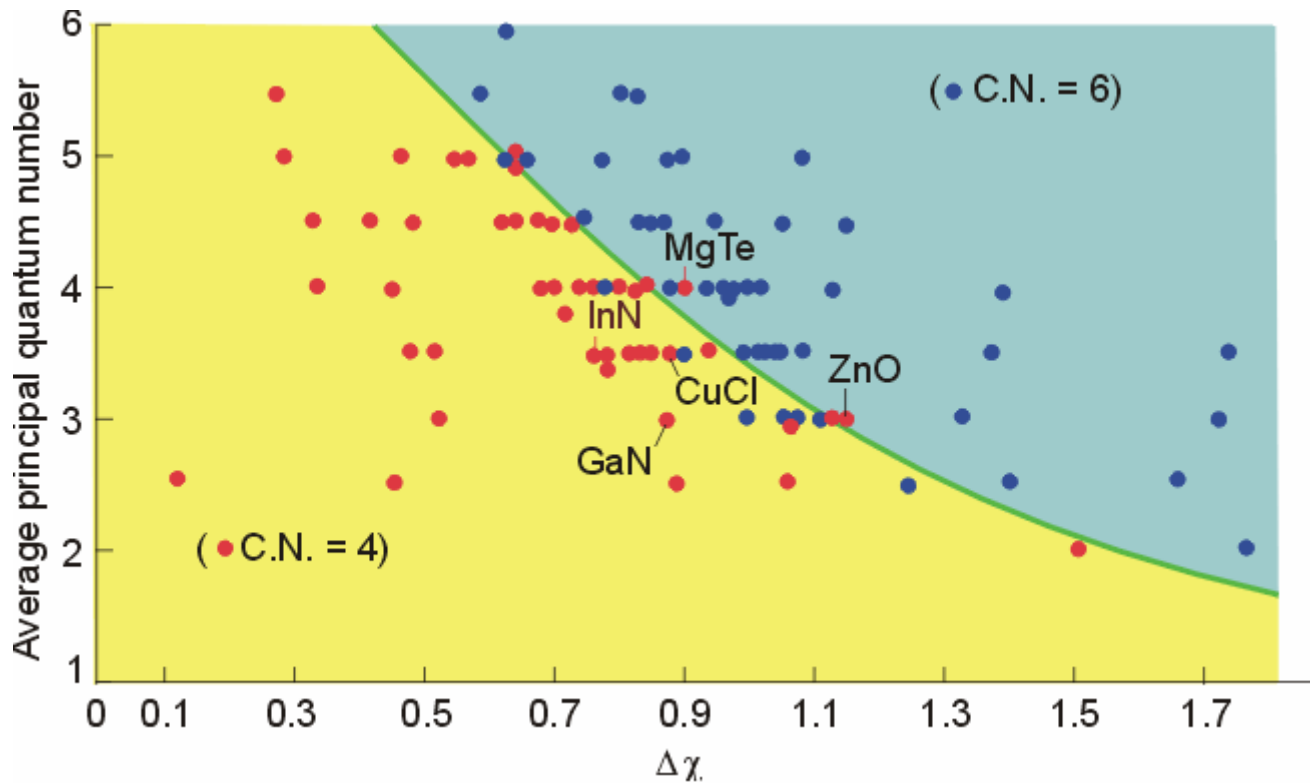


Figure 5.12 Plot of crystal radii r_M and r_X to show the sorting of structures for MX compounds using ratio rules (solid lines) and by areas of predominant structures (dashed lines). The original source included 95 compounds. (Reproduced with permission from J. K. Burdett, S. L. Price, and G. D. Price, *Solid State Commun.* **1981**, 40, 923. Copyright © 1981, Pergamon Press, Ltd., Headington Hill Hall, Oxford OX3 OBW UK.)

Increasing covalency



A Structural Map for compounds of MX

Table 5.6 Structures of some compounds of the type MX_2 and M_2X

| <i>Fluorite</i> (CaF_2) | | | <i>Rutile</i> (TiO_2) | | | <i>Antifluorite</i> | | | |
|------------------------------------|----------------|----------------|----------------------------------|----------------|----------------|-----------------------|-----------------------|------------------------|------------------------|
| CaF_2 | CdF_2 | ZrO_2 | MgF_2 | NiF_2 | TiO_2 | Li_2O | Li_2S | Li_2Se | Li_2Te |
| SrF_2 | HgF_2 | ThO_2 | MnF_2 | ZnF_2 | MnO_2 | Na_2O | Na_2S | Na_2Se | Na_2Te |
| BaF_2 | PbF_2 | CeO_2 | FeF_2 | PdF_2 | MoO_2 | K_2O | K_2S | K_2Se | K_2Te |
| BaCl_2 | | UO_2 | CoF_2 | | GeO_2 | Rb_2O | Rb_2S | | |
| | | | | | SnO_2 | | | | |

Table 2.3 Compounds with particular crystal structures

| Crystal structure | Example* |
|-----------------------------|---|
| Antifluorite | K_2O , K_2S , Li_2O , Na_2O , Na_2Se , Na_2S |
| Cesium chloride | CsCl , CaS , $TlSb$, $CsCN$, $CuZn$ |
| Fluorite | CaF₂ , UO_2 , $BaCl_2$, HgF_2 , PbO_2 , |
| Nickel arsenide | NiAs , NiS , FeS , $PtSn$, CoS |
| Perovskite | CaTiO₃ , $BaTiO_3$, $SrTiO_3$ |
| Rock salt | NaCl , $LiCl$, KBr , RbI , $AgCl$, $AgBr$, MgO , CaO , TiO , FeO , NiO , $SnAs$, UC , ScN |
| Rutile | TiO₂ , MnO_2 , SnO_2 , WO_2 , MgF_2 , NiF_2 |
| Sphalerite (zinc blende) | ZnS , $CuCl$, CdS , HgS , GaP , $InAs$ |
| Wurtzite | ZnS , ZnO , BeO , MnS , AgI , [†] AlN , SiC , NH_4F |

*The substance in bold type is the one that gives its name to the structure.

[†]Silver iodide is also found with a sphalerite structure, which is metastable.

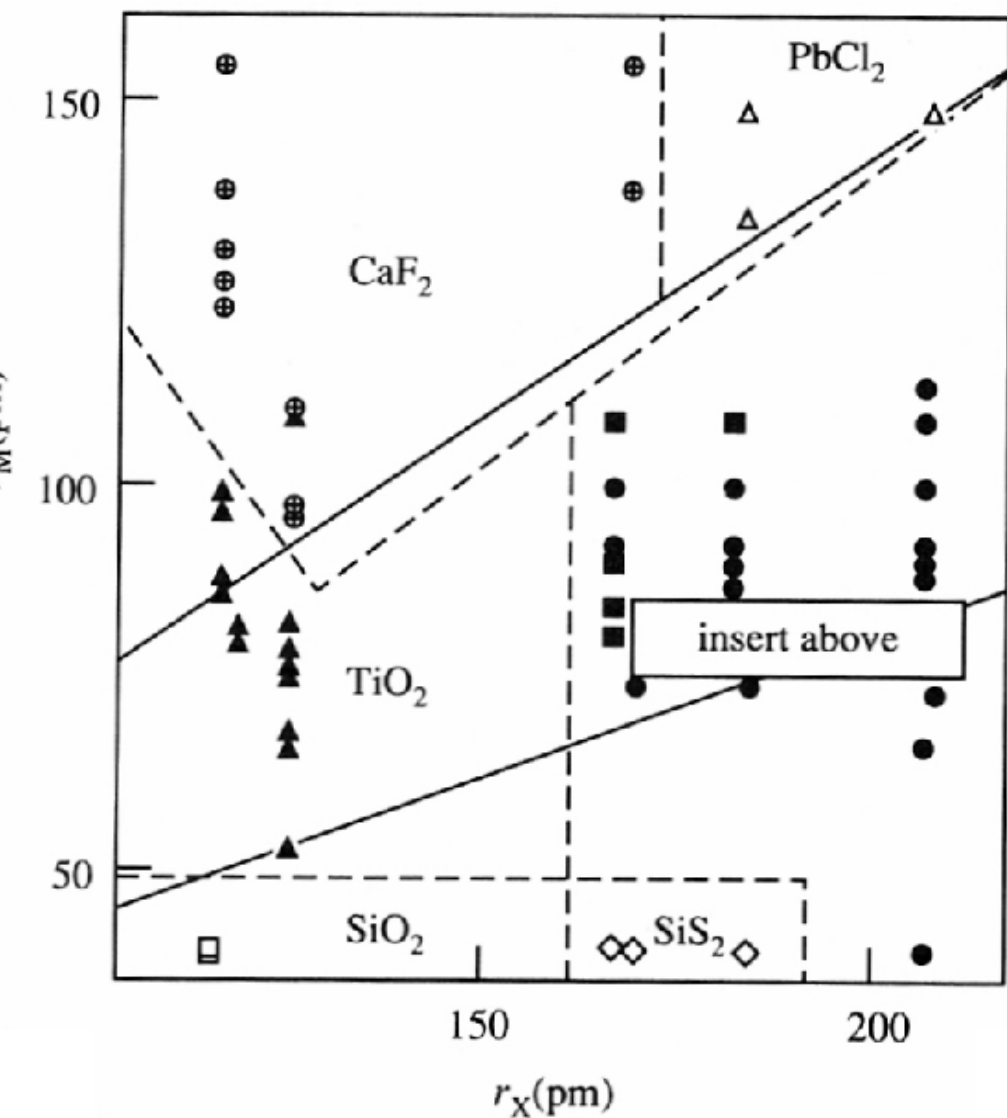


Figure 5.13 Plot for r_M and r_X to show the sorting of structures for MX_2 compounds using ratio rules (solid lines) and by areas of predominant structures (dashed lines). (Adapted with permission from J. K. Burdett, S. L. Price, and G. D. Price, *Solid State Commun.* **1981**, 40,

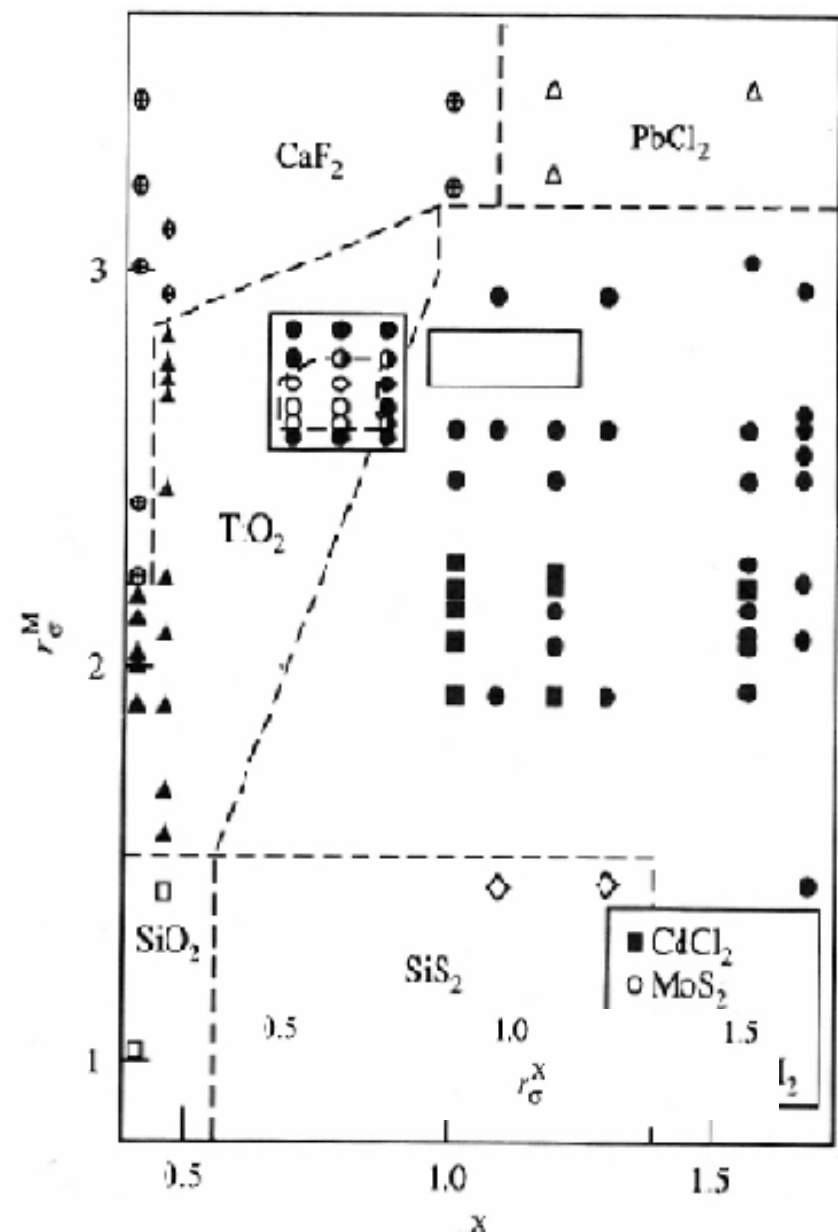
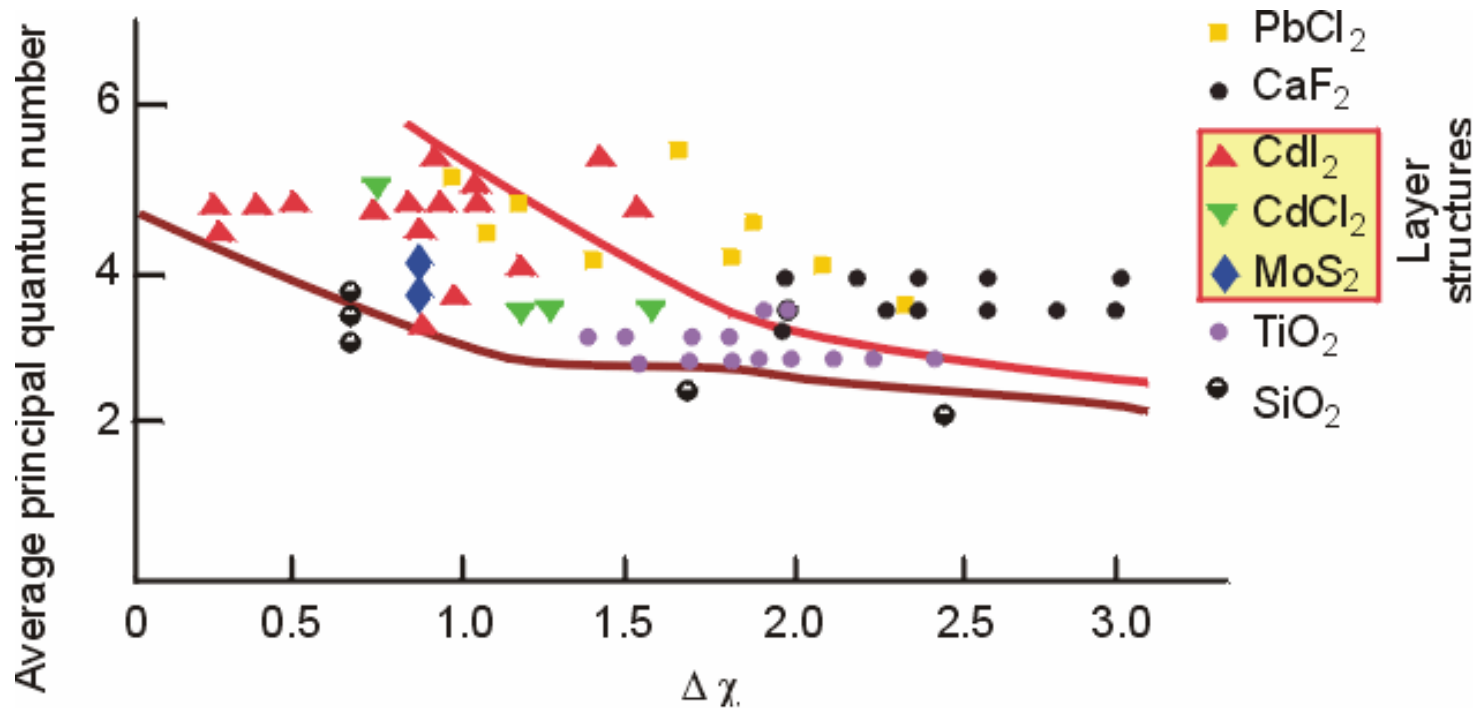


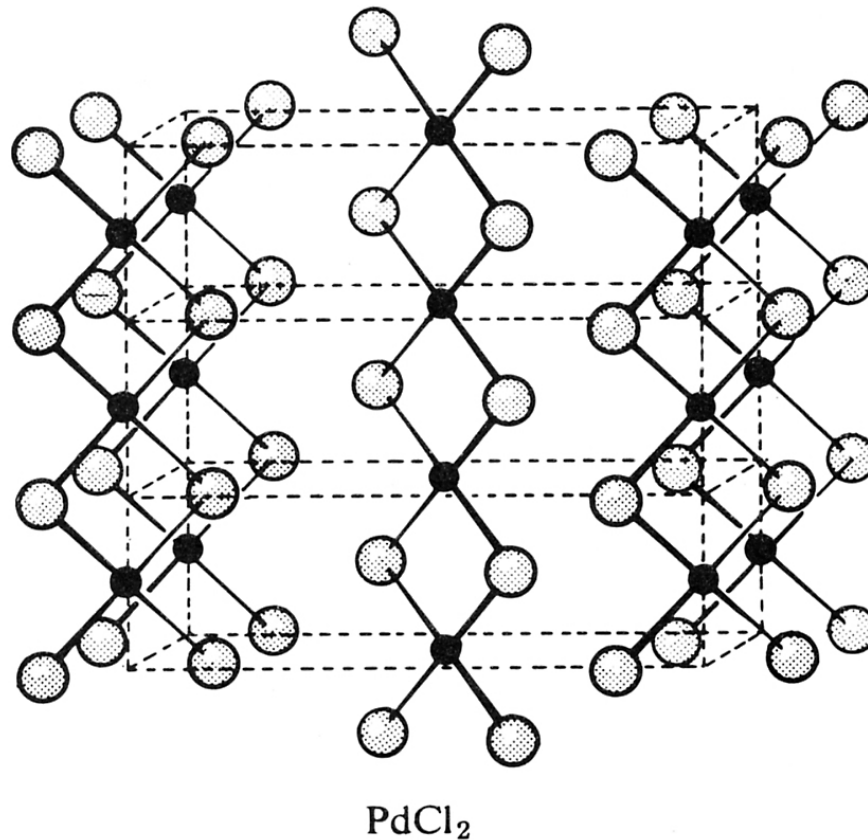
Figure 5.14 Sorting map of structures of MX_2 compounds plotting r_{σ}^M and r_{σ}^X (see text). The original reference included 113 compounds. The insert, drawn to a different scale, shows series sulfides, selenides, and tellurides in three vertical columns. (Adapted with permission from J. K. Burdett, S. L. Price, and G. D. Price, *Solid State Commun.* **1981**, *40*, 923. Copyright © 1981, Pergamon Press, Ltd., Headington Hill Hall, Oxford OX3 0BW UK.)

Increasing covalency

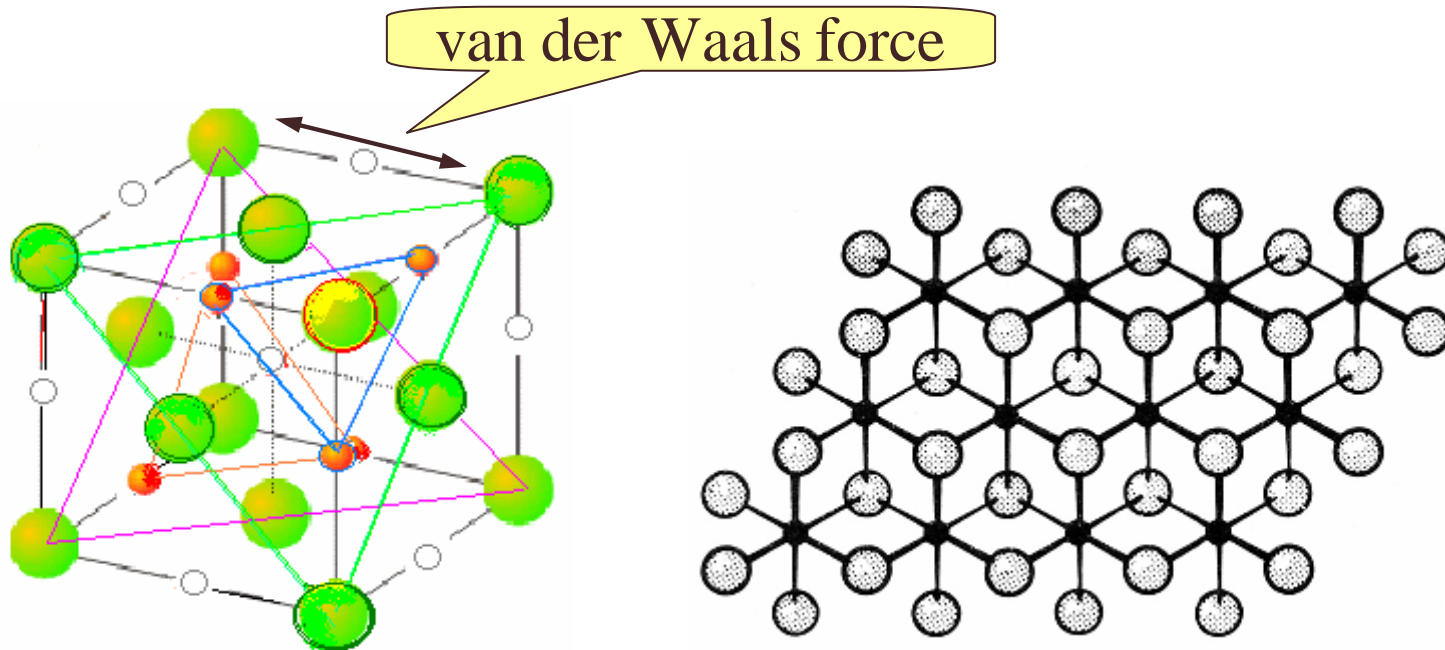


A Structural Map for compounds of MX_2

Salts of **highly polarizing cations** and **easily polarizable anions** have **layered structures**.



Salts of highly polarizing cations and easily polarizable anions have **layered structures**.

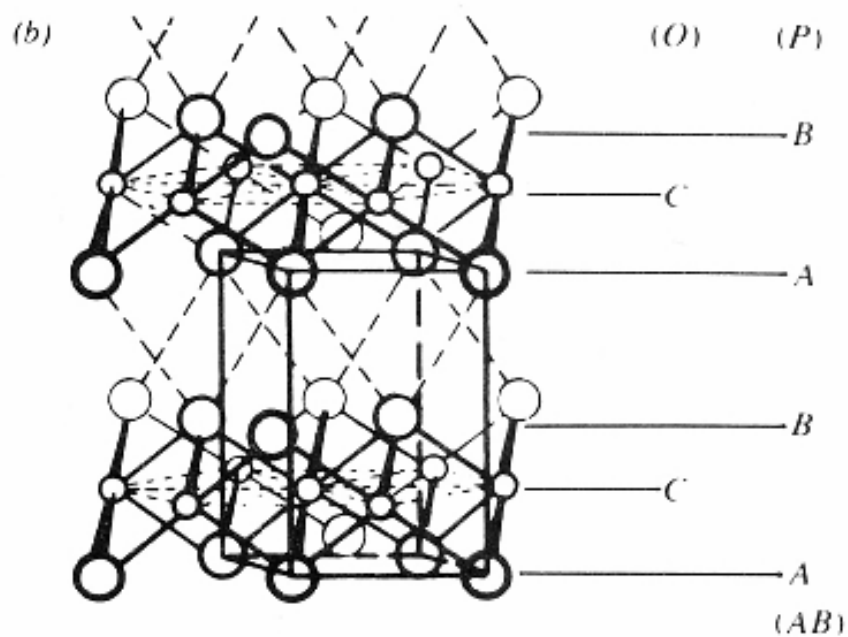


CdCl₂

Cl⁻ at ccp

Cd²⁺ at 1/2 O_h sites

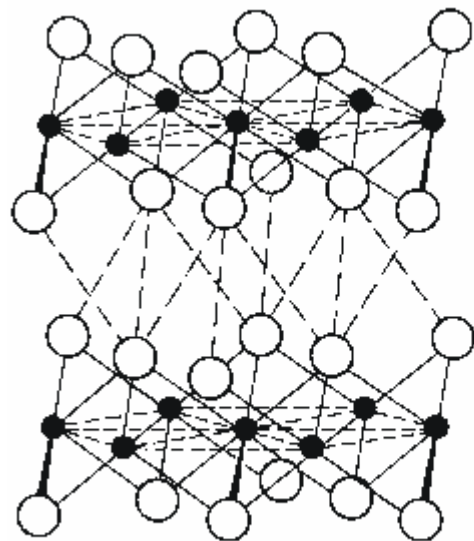
(alternate O layers)



CdI₂

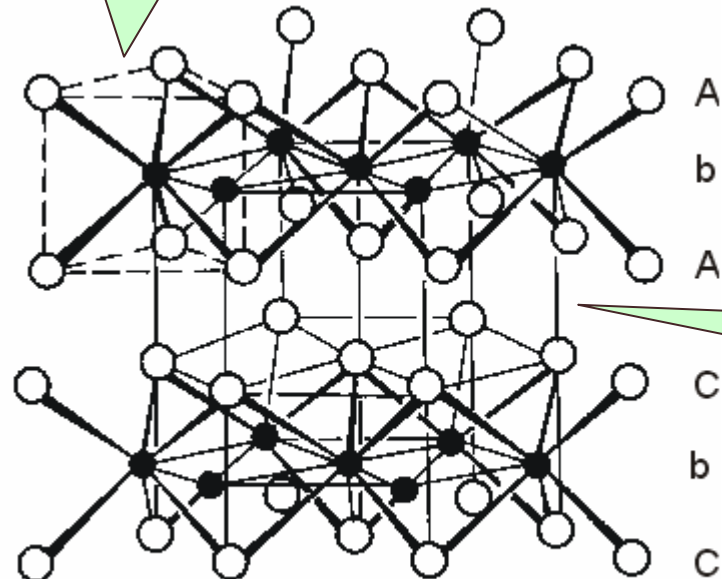
I⁻ at hcp

Cd²⁺ at $\frac{1}{2}$ O_h sites
(alternate O layer)



(a) ● Ta ○ S

298pm



(b) ● Mo ○ S

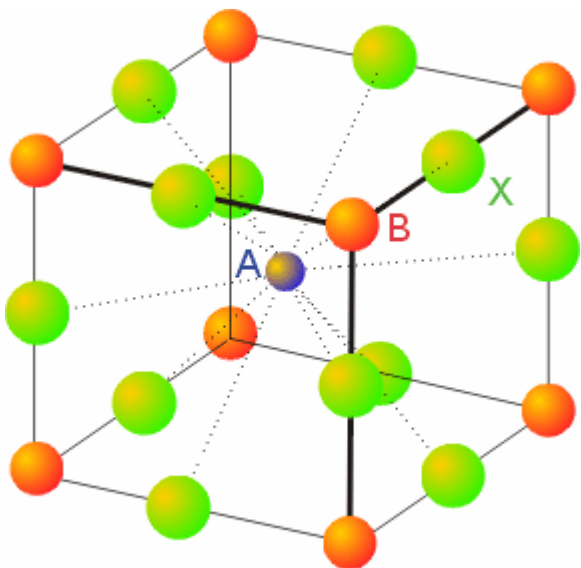
366pm

MoS₂

Mo⁴⁺ at hcp

S²⁻ at T_d sites

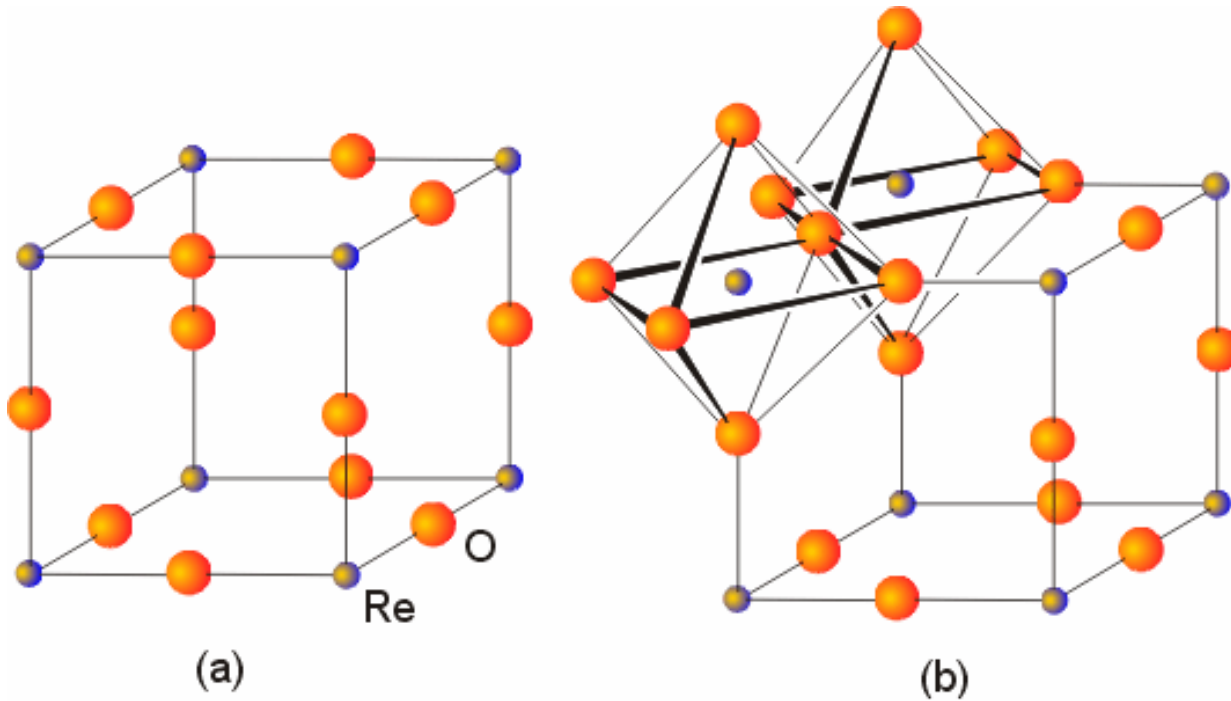
Unit Cell of Perovskite CaTiO_3



A and O together at ccp
B at $1/4 \text{ O}_h$ holes

Coord. #: A: 12; B: 6
atom/ unit cell
A: B: O= 1: 1: 3

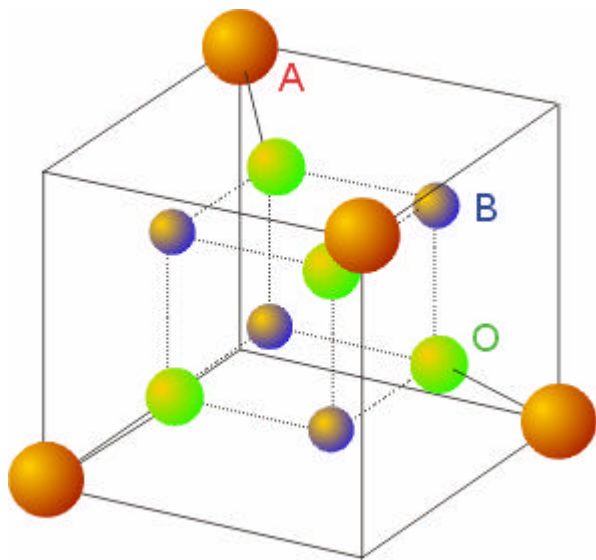
Unit Cell of ReO_3



Perovskite structure CaTiO_3 without Ca

Unit Cell of Spinel

MgAl_2O_4



Normal Spinel



O²⁻ at fcc

A at 1/8 T_d holes

B at 1/2 O_h holes

Inverse Spinel



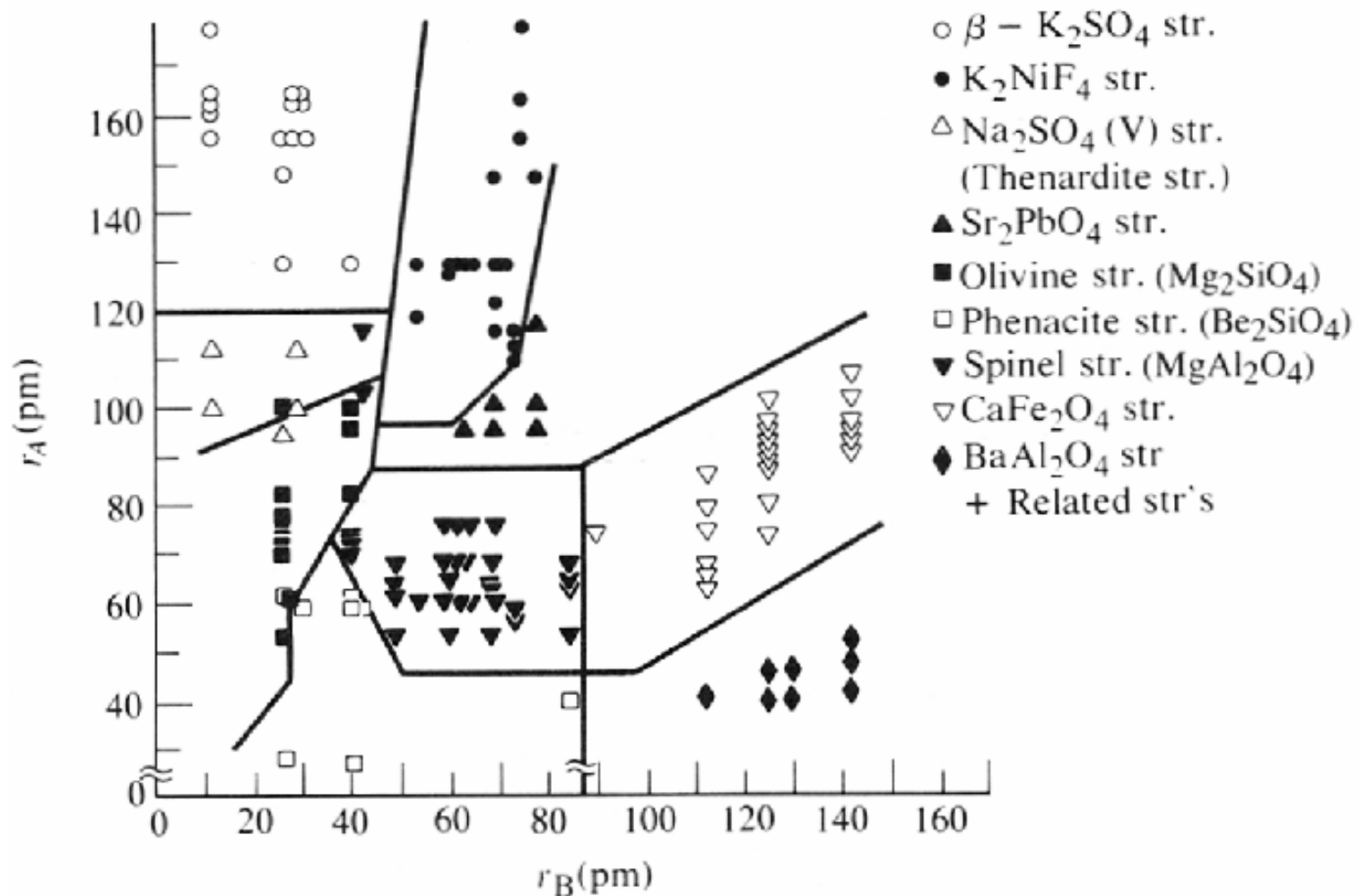
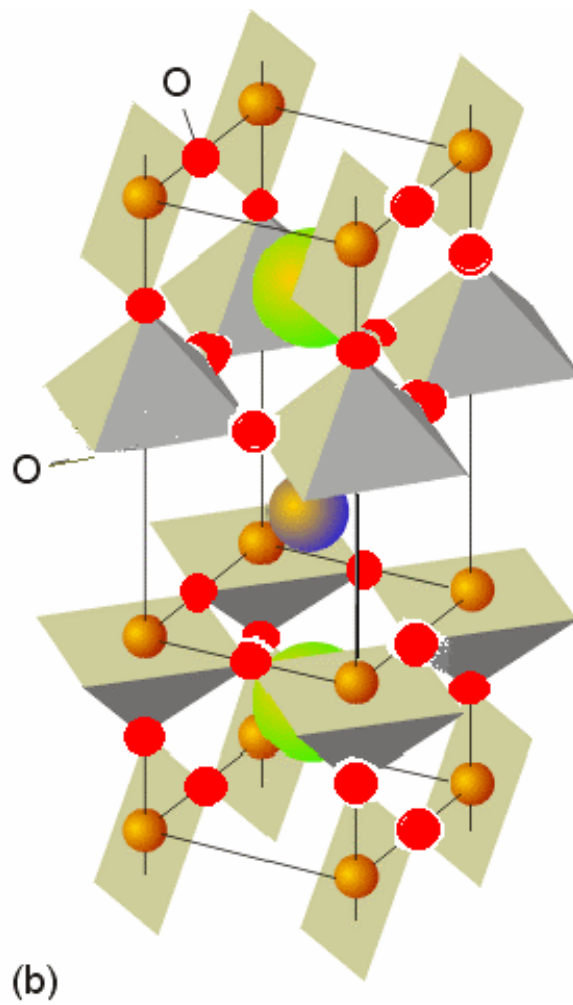
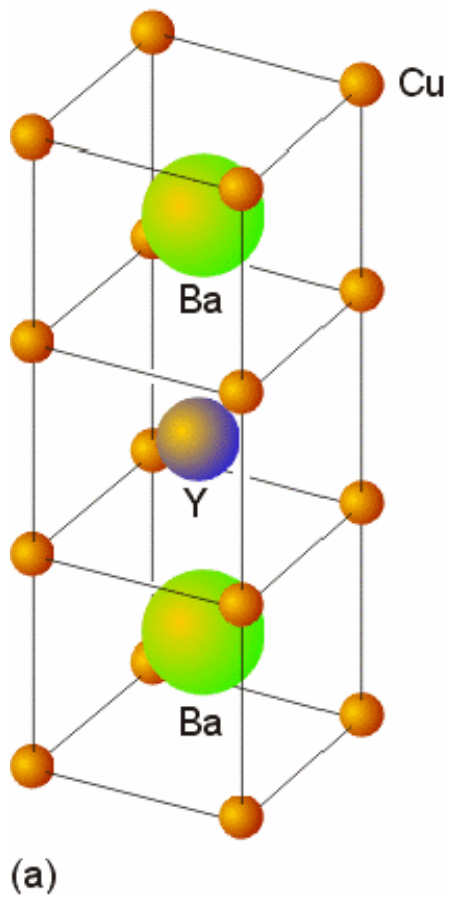
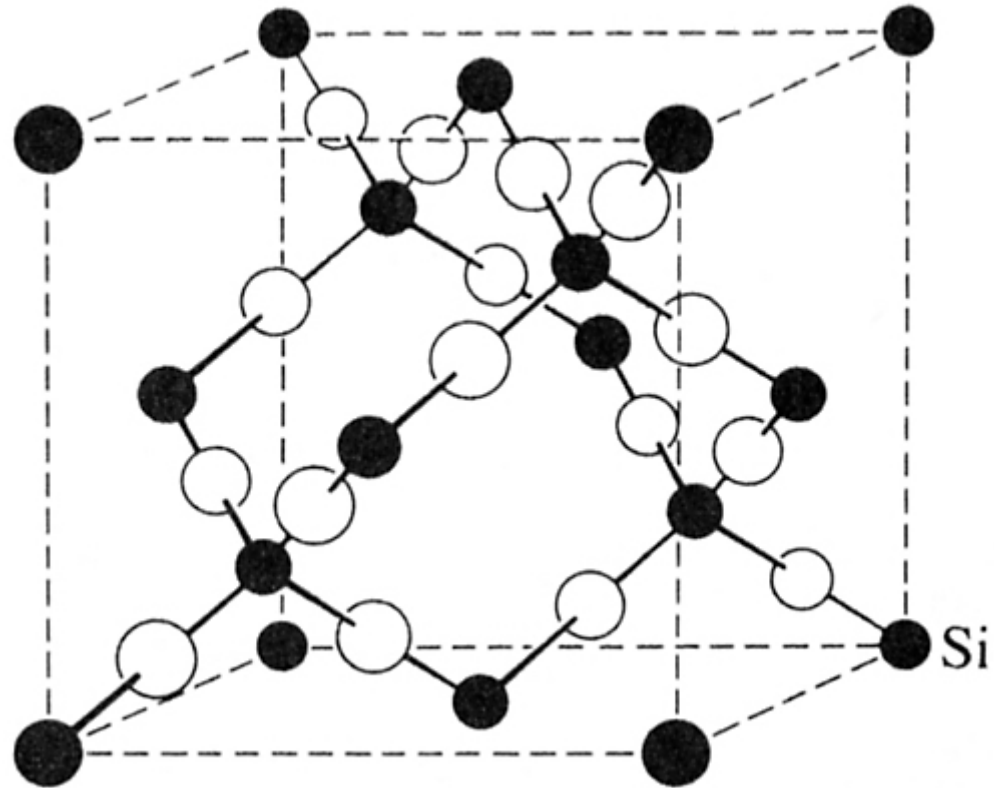


Figure 5.15 Structures of AB_2O_4 compounds. (Reproduced with





Quartz SiO_2

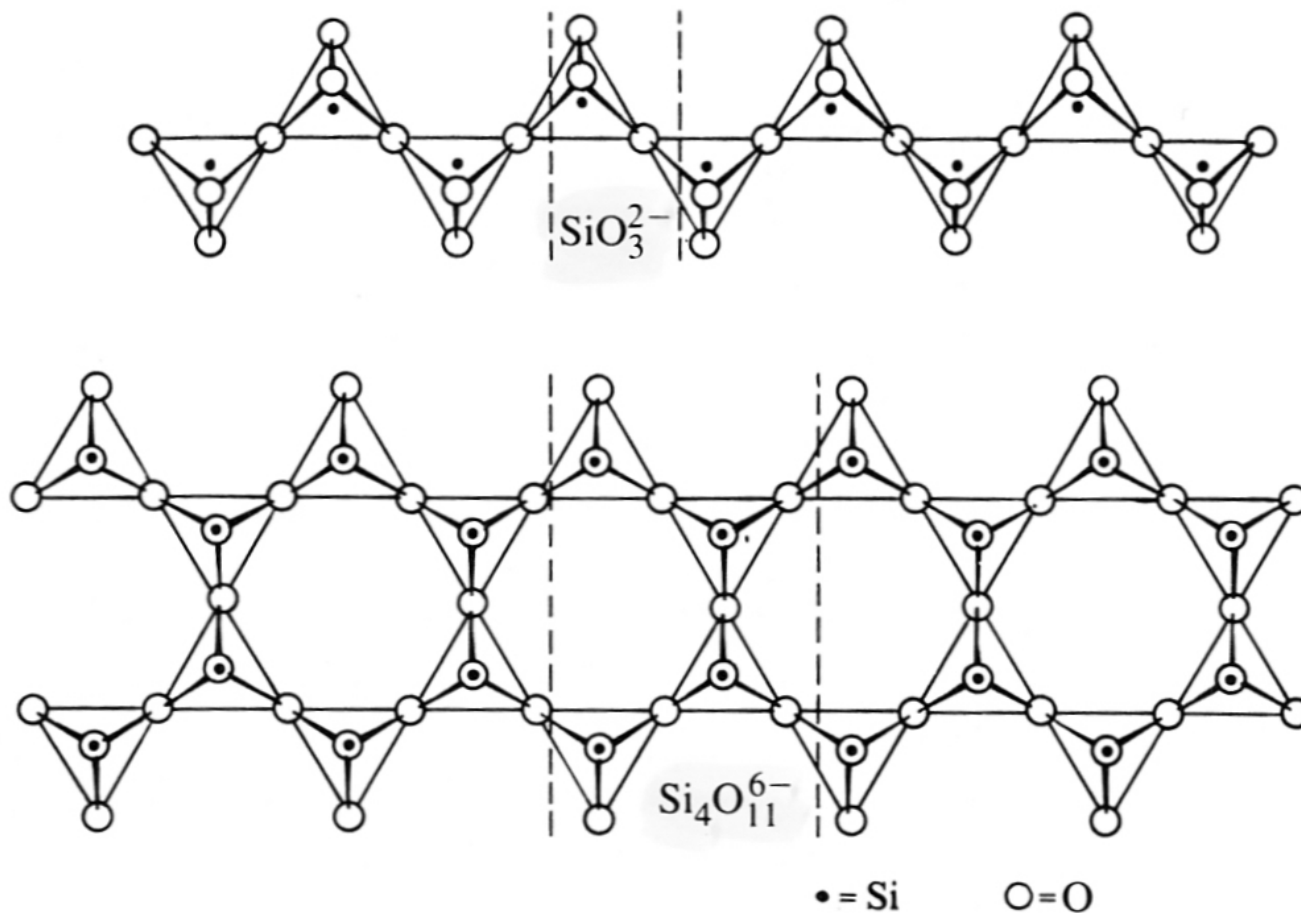
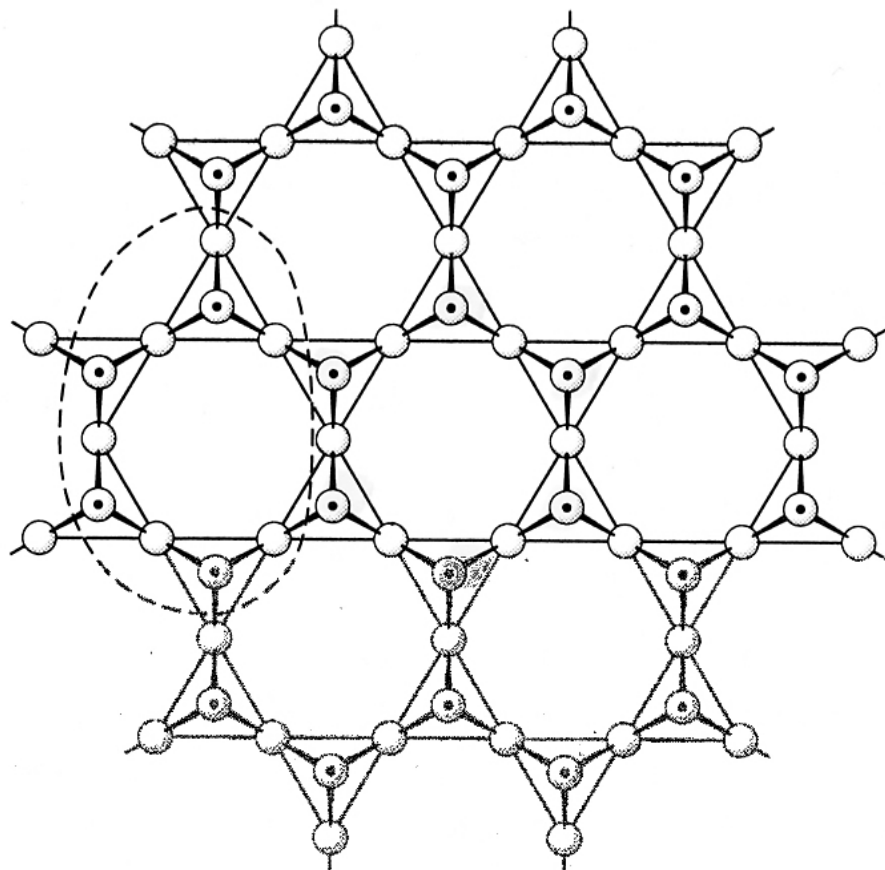
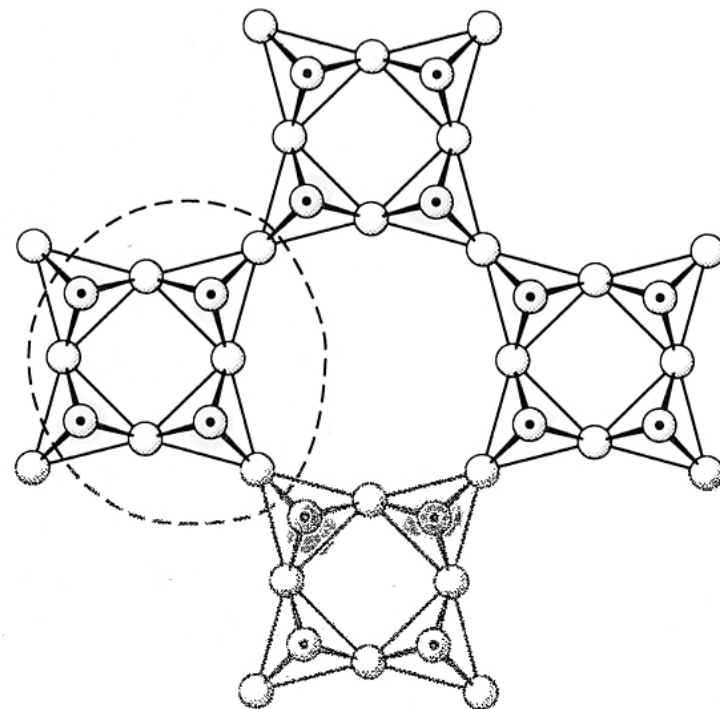


Figure 5.26 Chains of SiO_4 tetrahedra in (a) pyroxenes (repeating unit SiO_3^{2-}) and (b) amphiboles (repeating unit $\text{Si}_4\text{O}_{11}^{6-}$). The tetrahedra for b are viewed down one O—Si bond, where Si(\bullet) is below the O (\circ). The repeating units are marked by dashed lines.

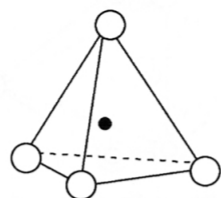


(a)

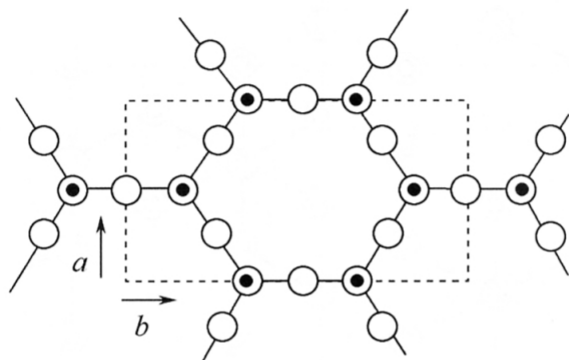


(b)

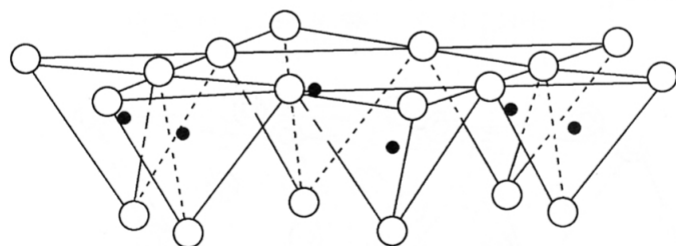
Figure 5.27 Sheets of SiO_4 tetrahedra. (a) Rings of six SiO_4^{2-} units in talc, $\text{Mg}_3[(\text{OH})_2|\text{Si}_4\text{O}_{10}]$, and biotite, $\text{K}(\text{Mg}, \text{Fe})_3[(\text{OH})_2|\text{AlSi}_3\text{O}_{10}]$. (b) Alternating rings of four and eight SiO_4 units in apophyllite. The repeating $\text{Si}_4\text{O}_{10}^{4-}$ is outlined.



(a) 單個矽氧四面體



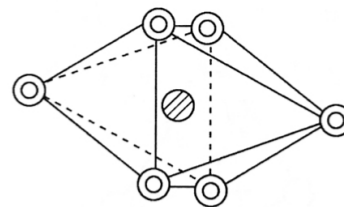
(b) 矽氧四面體晶片 (俯視圖)



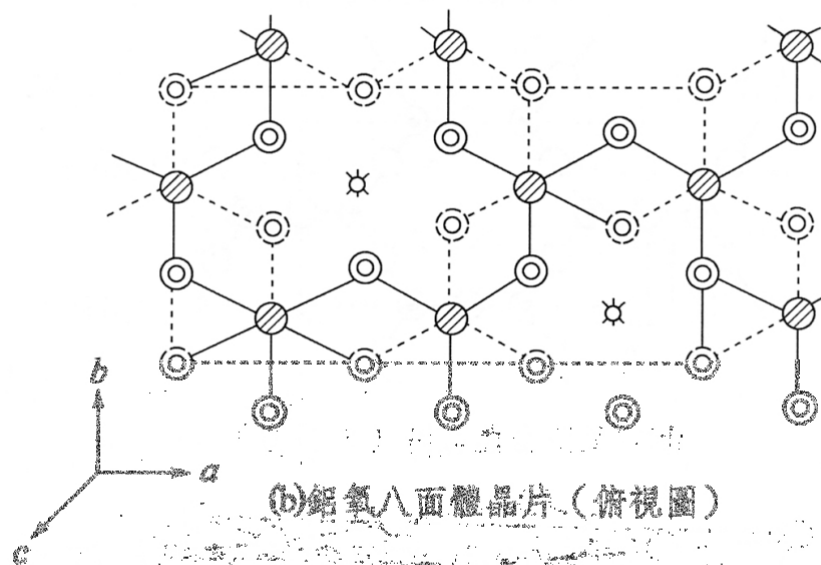
(c) 矽氧四面體晶片 (立體圖)

○ 氧 ● 矽

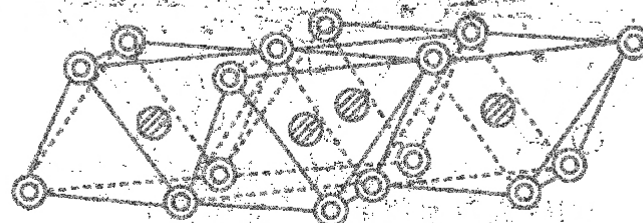
圖 2-1-1 矽氧四面體及矽氧四面體晶片示意圖



(a) 單個鋁氧八面體



(b) 鋁氧八面體晶片 (俯視圖)



(c) 鋁氧八面體晶片 (立體圖)

☆ 空餘位置 ⊗ 鋁 ⊙ 氫氧根 ⊕ 氫氧根

圖 2-1-2 鋁氧八面體及鋁氧八面體晶片構造示意圖

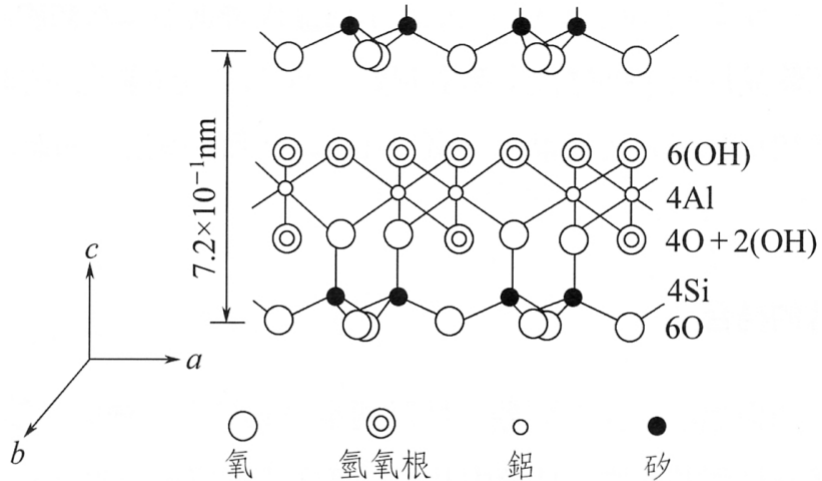


圖 2-1-3 高岭石晶體構造示意圖

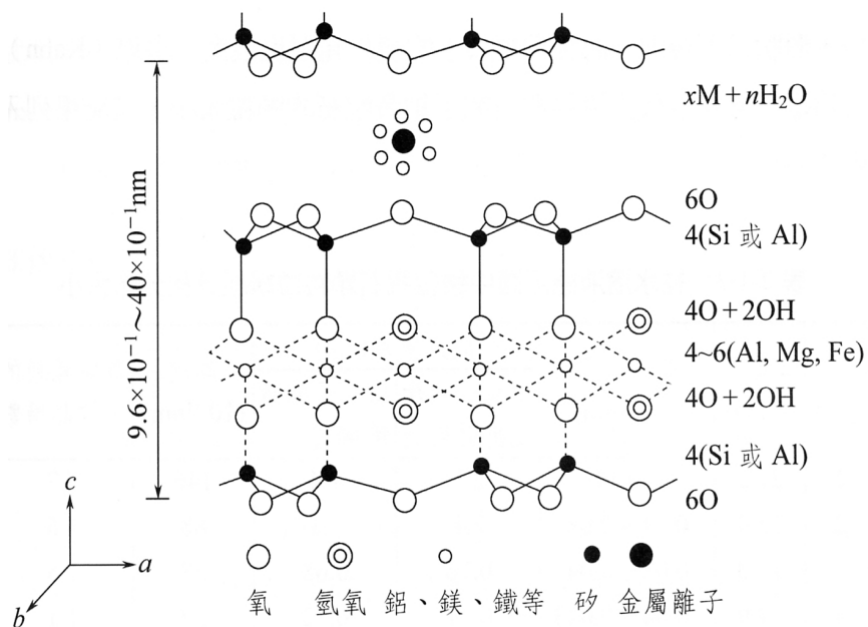
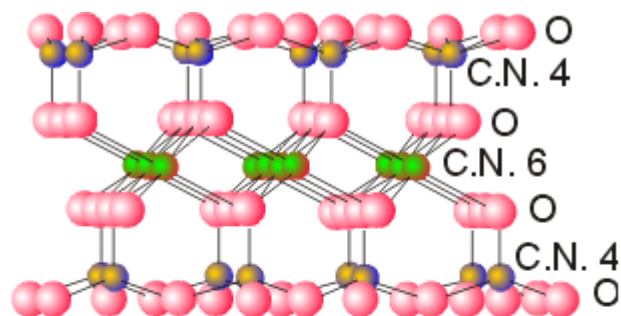
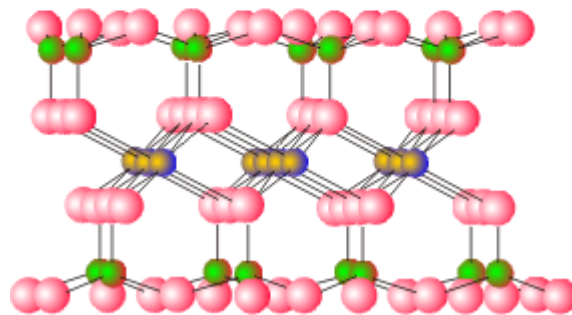


圖 2-1-5 蒙脫石晶體構造示意圖



(a)



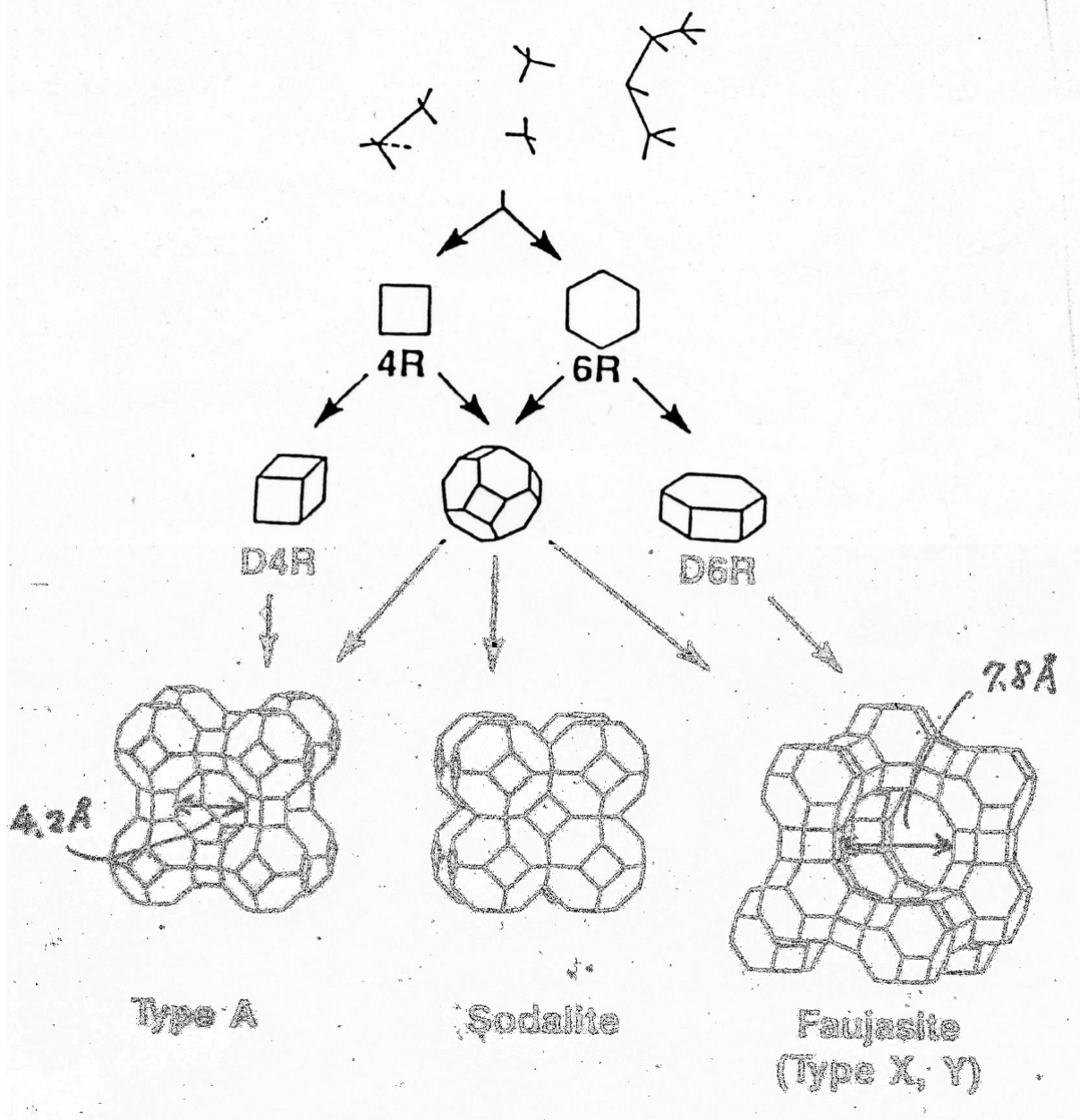
(b)

| Mineral | Ideal formula ^b | CEC ^c (meq/100 g) |
|--------------------------------|---|---------------------------------|
| Di octahedral minerals | | |
| Pyrophyllite | $\text{Al}_2(\text{Si}_4\text{O}_{10})(\text{OH})_2$ | 0 |
| Montmorillonite | $\text{Na}_x(\text{Al}_{2-x}\text{Mg}_x)(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot z\text{H}_2\text{O}$ | 60 - 120 |
| Beidellite | $\text{M}_x(\text{Al}_2)(\text{Al}_x\text{Si}_{4-x}\text{O}_{10})(\text{OH})_2 \cdot z\text{H}_2\text{O}$ | 60 - 120 |
| Nontronite | $\text{M}_x(\text{Fe}^{3+}, \text{Al})_2(\text{Al}_x\text{Si}_{4-x}\text{O}_{10})(\text{OH})_2 \cdot z\text{H}_2\text{O}$ | 60 - 120 |
| Tri octahedral minerals | | |
| Talc | $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$ | 0 |
| Hectorite | $(\text{Na}_2\text{Ca})_{x/2}(\text{Li}_x\text{Mg}_{3-x})(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot z\text{H}_2\text{O}$ | 60 - 120 |
| Saponite | $\text{Ca}_{x/2}\text{Mg}_3(\text{Al}_x\text{Si}_{4-x}\text{O}_{10}) \cdot z\text{H}_2\text{O}$ | 60 - 120 |
| Sauconite | $\text{M}_x(\text{Zn}, \text{Mg})_3(\text{Al}_x\text{Si}_{4-x}\text{O}_{10}) \cdot z\text{H}_2\text{O}$ | |

a: Only major cations are shown.

b: x depends on the origin of the mineral; montmorillonites can show a degree of substitution x in the octahedral sheet in the range 0.05- 0.52. Natural samples generally show substitutions in both octahedral and tetrahedral sheets, which renders the real situations more complex.

c: Cation-exchange capacity.



Structure of synthetic zeolite ZSM-5

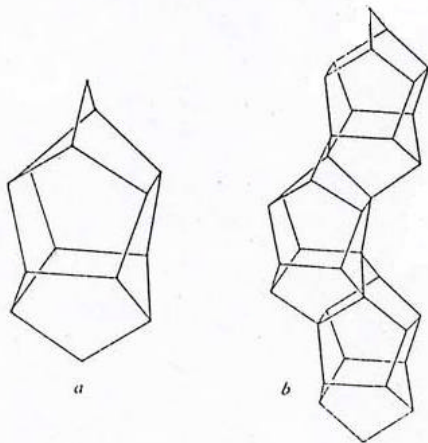


Fig. 1 Characteristic configuration (a) and its linkage within chains (b) in ZSM-5. These chains run parallel to [001]. Only T-atoms (Si, Al) are shown.

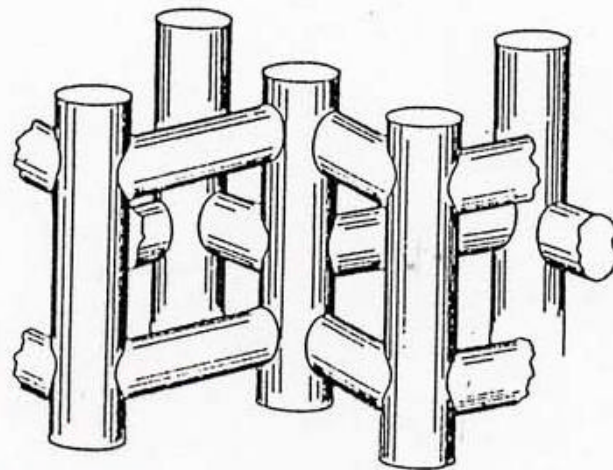


Fig. 4 The channel structure in ZSM-5.

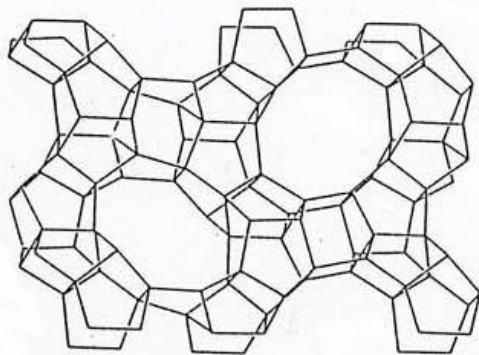


Fig. 2 Skeletal diagram of the (010)-face of the ZSM-5 unit cell. The x-axis is horizontal and the z-axis vertical. Oxygen atoms are not shown. The 10-membered ring apertures shown are the entrances to the straight channels which run parallel to [010].

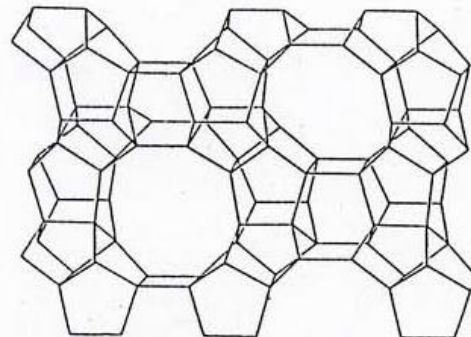


Fig. 3 Skeletal diagram of the (100)-face of the ZSM-5 unit cell. The y-axis is horizontal and the z-axis is vertical. Oxygen atoms are not shown. The nearly circular 10-membered ring apertures shown are the entrances to the sinusoidal channels which run parallel to [100].

Table 5.14 Characteristics of some zeolites

| <i>Name</i> | <i>Formula</i> | <i>Oxygens in ring</i> | <i>Pore size (Å)</i> |
|-----------------------------|---|--------------------------------------|--------------------------------------|
| Zeolite A (Linde Type A) | $\{\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}] \cdot 27\text{H}_2\text{O}\}_8$ | 8 | 4.1 |
| Heulandite | $\text{Ca}_4[\text{Al}_8\text{Si}_{28}\text{O}_{72}] \cdot 24\text{H}_2\text{O}$ | $\begin{cases} 8 \\ 10 \end{cases}$ | 2.6×4.7 3.0×7.6 |
| Ferrierite | $\text{Na}_2\text{Mg}_2[\text{Al}_6\text{Si}_{30}\text{O}_{72}] \cdot 18\text{H}_2\text{O}$ | $\begin{cases} 8 \\ 10 \end{cases}$ | 3.5×4.8 4.2×5.4 |
| Silicalite (ZSM-5) | $\text{Na}_n[\text{Al}_n\text{Si}_{96-n}\text{O}_{192}] \cdot \sim 16\text{H}_2\text{O}$ | $\begin{cases} 10 \\ 10 \end{cases}$ | 5.3×5.6 5.1×5.5 |
| Faujasite | $(\text{Na}_2, \text{Ca}, \text{Mg})_{29}[\text{Al}_{58}\text{Si}_{134}\text{O}_{384}] \cdot 240\text{H}_2\text{O}$ | 12 (3-dim.) | 7.4 |
| Linde Type L | $\text{K}_6\text{Na}_3[\text{Al}_9\text{Si}_{27}\text{O}_{72}] \cdot 21\text{H}_2\text{O}$ | 12 | 7.1 |
| Mordenite | $\text{Na}_8[\text{Al}_8\text{Si}_{40}\text{O}_{96}] \cdot 24\text{H}_2\text{O}$ | $\begin{cases} 12 \\ 8 \end{cases}$ | 6.7×7.0 2.6×5.7 |